

# Quartz: Deposits, Mineralogy and Analytics

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# Chapter 2

## Assessment of High Purity Quartz Resources

Reiner Haus, Sebastian Prinz and Christoph Priess

**Abstract** Very high purity quartz for advanced high-tech applications is currently sourced from just a few locations around the world. Such is the expected growth in demand that more sources are required to be found. For successful high purity raw quartz resource identification detailed analysis and appropriate process technology selection is essential. This article reviews general aspects of high purity quartz deposits, exploration requirements, quality evaluation of raw quartz, and provides basic insight into the different specifications and market developments of the high-tech end-user industries reliant on very high purity refined quartz products.

### 2.1 Introduction

Quartz is one of the most abundant minerals. It occurs in many different settings throughout the geological record (Götze 2009). As the prime source of silica the mineral has wide large volume application in the manufacture of glass, ceramics, refractory materials and other traditional uses (Blankenburg et al. 1994). However, only very few deposits are suitable in volume, quality and amenability to tailored refining methods for speciality high purity applications. As such high purity quartz has become one of today's key strategic minerals with applications in high-tech industries that include semiconductors, high temperature lamp tubing, telecommunications and optics, microelectronics, and solar silicon applications (Blankenburg et al. 1994; Haus 2005, 2010; Moore 2005; Dal Martello et al. 2011a, b).

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Whilst most processing plants for standard quartz applications deploy off-the-shelf technology solutions, quartz for high-tech applications requires tailored processing techniques and specially designed equipment to achieve essential high purity specifications. Beneficiation of raw quartz into refined high-purity products involves several refinement steps which need to be adapted to effectively minimise the specific impurities of the individual raw quartz feed to comply with stringent end-use specifications (Haus 2005). As a result, high purity quartz with total impurity levels less than 20 ppm may be achieved so creating a highly valuable raw material which commands up to 5 EUR/kg.

## 2.2 Present Quartz Supplying Countries

Globally, the export of lump quartz has been diminishing for a variety of reasons. Both suppliers and consumers increasingly require quartz granules with the highest quality specifications. This is beneficial for suppliers who add more value to the quartz product by improving refining techniques. For consumers it saves processing cost and enables them to concentrate on their core business instead of investing in purifying steps to improve the raw material.

Today, US-based Unimin Corp./Sibelco still dominates the global high purity quartz market from operations in North Carolina, USA. One of the few alternative suppliers, Norsk Mineral's Norwegian Crystallites has been producing high purity quartz from its Drag plant in western Norway and several underground and open pit mines since mid-1996 when the company changed ownership. In 2011 Imerys SA has combined its US-based Spruce Pine companies KT Feldspar and The Feldspar Corp. (TFC) with Norwegian Crystallites now owned and operated by The Quartz Corp, a joint venture between Imerys and Norsk Mineral.

Potential new entrants into the high purity quartz world market are still under development. Moscow-based JSC Polar Quartz (Moore 2005) has raw material supplies based on quartz deposits on the eastern slopes of the sub-polar Ural Mountains and Kyshtym Mining's (KGOK) crystal quartz deposit is situated on the eastern slopes of the South Ural Mountains. In the Soviet era Kyshtym's plant supplied 60% of domestic high purity quartz demand used to make clear glass for microelectronics and optical applications. Little is known about Chinese Donghai Pacific Quartz although it is understood to serve domestic markets.

In the early 1970s Brazil was the world's main supplier of high purity quartz based on lascas; a term used to describe manually beneficiated rock crystal. Up to 1974, when the Brazilian government imposed an embargo on exports of lump quartz, export levels rose to in excess of 10,000 tpa. Brazil appears to have irretrievably lost its position in the quartz consuming world. Additionally, its infrastructure does little to attract investment of the foreign capital necessary to develop the quartz industry over the medium term. It is also known that the Brazilian high quality quartz materials show considerable variations in quality compared with raw quartz from deposits in other parts of the world. This inhibits the resurrection

and further development of Brazilian quartz for high quality products. Potential deposits in Madagascar and Angola also suffer from poor infrastructure and lack of interest on the part of their governments.

In Asia, Japan's influence is large especially in Southeast India and in Sri Lanka. Japan once imported quartz lumps from these regions. However, government-led efforts on the part of the quartz supplier countries were launched to stop the export of unrefined quartz lumps and to support the development of quartz processing within the country. Today these countries specialise in the production of high purity filler materials for epoxy moulded compounds (EMC) low in uranium and thorium used in the manufacture of computer chips.

Given its strategic relevance to the semiconductor and photovoltaic industries many more high purity quartz deposits are under development. However, the exploration and exploitation of new suitable quartz deposits is hampered by quality assurance regulations, which are globally applied. Whilst traditional sources of quartz have been questioned in quality terms, it is in their interest to demonstrate that their material is tested and meets the standards of silica glass production. Suppliers from new quartz deposits have yet to achieve this status. This is achieved normally in several consecutive cycles of tests with increasing quantities of test material. These tests must be carried out for many of the product groups in the various application areas.

These pre-business services are expensive but made necessary by increasingly strict quality regulations. They require certain personnel expertise from the potential new suppliers (e.g. for the provision of relevant raw material) and highly specialised cooperation partners well recognised within the industry.

## 2.3 Typical High Purity Quartz Applications

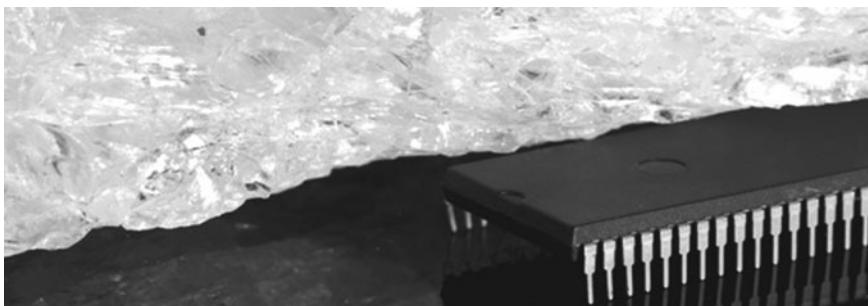
As mentioned in the introduction the applications of high purity quartz in the high tech industries are manifold. Main applications are in the semiconductor, high temperature lamp tubing, telecommunication and optics, microelectronics, and solar silicon industries.

The semiconductor industry places the most stringent requirements on quartz purity. From single crystal silicon growth in quartz crucibles via the Czochralski process to the handling and processing of wafers in clean rooms, high purity quartz ware is employed. Fused quartz is the basic material for quartz ware used in the semiconductor industry since it combines excellent high temperature properties (i.e. thermal shock resistance and thermal stability) and high purity in a unique way. It withstands the high temperature gradients and high rates of heat transfer in rapid thermal processing which are commonly applied to wafers in order to modify their properties. The high purity of the quartz prevents contamination of wafers during the different processing steps.

The application of high purity quartz as basic material in high temperature lamp tubing takes advantage of its high transmission characteristic and its exceptional



**Fig. 2.1** High temperature Xenon lamp made from high purity quartz



**Fig. 2.2** High purity quartz is applied as filler material in epoxy moulding compounds (EMC) used as cover in the microelectronics chip production

thermal shock resistance and thermal stability. It is used in the high performance, high temperature lamp manufacturing sectors for UV lamps, mercury, xenon and halogen bulbs, and high intensity discharge lamps (Fig. 2.1).

Silica glass is widely used as basic material for optical fibers and additional optoelectronic devices in the telecommunications industry. It is used in the optical industry in microlithographic applications, excimer laser optics, beamers and other specialised applications. In the microelectronics industry, a major application is as filler material in epoxy moulding compounds (EMC) for electronic components (Fig. 2.2).

Silicon is the most common material for the production of solar cells in the photovoltaic industry either in mono- or polycrystalline form.

Specific requirements as to tolerable limiting values differ from industry to industry. In the lamp tubing and optics industries aluminium content in the refined

quartz concentrate should not exceed 20 ppm, other metals should be less than 1 ppm, and total impurities less than 30 ppm. For semiconductor base materials and crucibles aluminium content should be even lower, specified to less than 10 ppm, other metals less than 0.1 ppm, and total impurities not to exceed 15 ppm.

Feedstock for solar silicon used in the photovoltaic industry should generally have boron and phosphorus contents in the sub-ppm range since these elements are most difficult to remove and negatively affect the performance of the solar cells (Geerligs et al. 2002).

For microelectronics applications, e.g. in epoxy moulding compounds, uranium and thorium, both responsible for soft errors by alpha radiation, should be less than 2 ppb, and in low alpha applications, even less than 0.5 ppb.

## 2.4 Demand Situation

The global outlook for high purity quartz using industries is still positive with growth rates between 3 and >5%, specifically in certain lighting, semiconductor and photovoltaic applications.

### 2.4.1 *Lighting Industries*

In the USA, the EU and many more countries the sale of general service incandescent lamps is banned. Compact fluorescent lamps (CFLs) are expected to replace most of them owing to government advice. Demand for CFLs will surge more than 20% annually through 2013 as consumers transfer to the new technology. However, halogen lamps are also forecast to grow especially fast through 2013, as, they will benefit from the ban too. Although less efficient and shorter-lived than CFLs, halogen lamps outperform CFLs in terms of colour rendering and they do not contain mercury. In addition, new halogen-based product inventions are already close to the energy efficiency of CFLs and fit well with general lamp connectors. Demand for halogen lamps will also benefit from recovering motor vehicle production levels, as they find widespread use in headlamps.

Metal halide lamps (Xenon) will lead the high intensity discharge (HID) product segment. As mercury vapour lamps are phased-out of the market, metal halide lamps will gain market share in outdoor lighting applications. Furthermore, metal halide lamps are increasingly finding use in high-end (premium cars) motor vehicle headlamps. Expectations of European lamp manufacturers are for growth rates in the 3–5% range worldwide over the next 3–5 years. Rapid development in the BRIC countries also supports these expectations.

Since both, halogen- and xenon-based lamps are made of high purity quartz glass to withstand the high temperatures and to offer high transmission characteristics as

well as exceptional shock resistance ([Chap. 3](#)), the demand in high purity quartz will benefit from the increasing demand in the lamp tubing and automotive industries.

### ***2.4.2 Semiconductor Industry***

The demand for high purity quartz products in the semiconductor industry is closely related to new fabrication plants (fabs) to be built, consuming most of the semiconductor base materials, as well as to the production of monocrystalline silicon (crucibles).

SEMI's World Fab Forecast ([www.semi.org](http://www.semi.org)) recently predicted steady growth in capacity, about 9% for 2011 and 7% for 2012. In 2010, about seven facilities were expected to begin construction; of these, five are considered high-volume fabs.

The outlook of 5.5% revenue growth for total fab materials is in-line with current expectations of modest single-digit growth for the semiconductor industry in 2011. Stronger demand for electronics, especially mobile products, could result in even higher than expected growth for semiconductor products in 2011; therefore increasing the amount of wafers processed and materials consumed.

The record levels for semiconductor sales, in both revenues and units, generated tremendous growth in the semiconductor materials market. Total silicon wafer shipments, from wafer suppliers to the fabs, grew 40% in 2010. Growth was strong for all wafer diameters. With the broad-based recovery in the semiconductor industry, both 150 and 200 mm shipments increased by rates comparable to those for 300 mm wafer shipments last year. Overall, 6% wafer shipment growth is currently estimated for 2011 with 300 mm shipments likely growing in the 11–13% range.

### ***2.4.3 Photovoltaic Industry***

In the solar industry all signs point to further growth in the coming years.

Production of c(crystalline)-Si in the 2007–2011 period saw CAGR of 45% while Si-production for 2010–2014 is forecast to slow to CAGR in the 20–30% range reaching 300,000–400,000 tpa in 2014 (2010: 170,000 tpa). In 2010 solar cell production was up 118%, compared with 2009, when more solar cells were produced than the combined total in all prior years.

Grid parity has now been achieved in a number of countries. Based on the demand in high efficiency cells, mono c-Si is expected to keep around 30% share at least for the next 3 years.

However, new multi-pulling production techniques (recharging) and larger diameters of the monocrystals will demand more voluminous crucibles, i.e. less crucible silica glass per kg of monocrystal produced (volume to area ratio). Hitherto, mainly small furnaces with crucible diameters between 16" and 22" were

used for PV applications. More recently, however, the same sizes for crucibles as are used in the semiconductor industry are being requested. Therefore, the increase in high-purity quartz granule consumption will not equal the upcoming growth in c-Si monocrystal production, but it is still estimated at above 5% p.a.

Manufacturers of solar silicon are looking to remain competitive by pushing production costs down. The result might be a process of consolidation: in 2012, the four largest producers alone—OCI, Hemlock, GCL and Wacker—could probably cover worldwide demand. Prices, which are currently still dominated by demand, should then fall and relate more to costs.

This could attract new technologies which are based on high purity materials and less investment and operating costs to enter the solar silicon market. On the other hand it will raise the demand in high quality quartz, specifically low in boron and phosphorus.

### ***2.4.4 Optical Fibers***

Requirement for continually improving broadband connections has increased demand for synthetic silica glass used in fibre optics for optical data transmission. In fibre optics almost all waveguides are made of synthetic quartz/silica, handles and leader corning, however, are manufactured of natural quartz.

## **2.5 Resource Estimation**

Expertise in geology, chemistry, and mineral processing is required to develop the full potential of a high purity quartz deposit. Related to the geological conditions at the time of formation, quartz often contains fluid and/or mineral inclusions (Roedder 1984; Rykardt 1995; Hyrsl and Niedermayr 2003; Heaney et al. 1994) that need to be removed to meet stringent requirements for high purity applications. In addition detailed information about structural impurities in quartz (Flem et al. 2002; Götze et al. 2004) are of interest since they may define the economic limits in purifying the raw quartz. In order to achieve maximum value, process technologies need to be adapted to the specific characteristics of each quartz deposit. Remnant fluids, from which quartz crystallised, occur trapped within individual crystals as do different types of mineral inclusions such as iron oxides, phosphates, silicates and heavy minerals. These inclusions need to be identified by analytical methods in order to determine what beneficiation processes will be used to remove them, as they are undesirable impurities that detract from the quality of potential quartz products.

Whilst chemistry is important in determining quartz quality it is equally important to identify quantity in order to determine how long, at a given production rate, a potential mine may produce economically viable product for at least, say, 20 years as a realistic resource/venture.



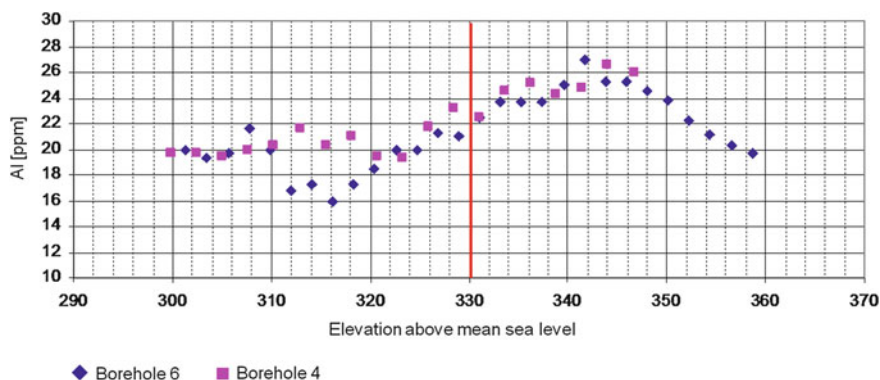


**Fig. 2.3** Typical vein quartz deposit (Africa), width of the picture approx. 15 m

Hydrothermal vein-like quartz deposits (Fig. 2.3) usually comprise zones reflecting different periods of mineralisation. Zones vary enormously in thickness, with individual quartz veins ranging from less than 1 up to 500 kt. Massive quartz deposits in similarly zoned pegmatites, essentially very coarsely crystalline hydrothermal host rock fissure fillings, are basically of larger volumes (up to 5 Mt) while metamorphic quartzite bodies are usually of even larger dimensions but of lower quality. In contrast, silica sand deposits are typically loosely consolidated and are of little prospect for economically viable high purity applications.

International standards, e.g. Australia's JORC or Canada's NI 43-101 codes, prescribe procedures to progressively identify, in terms of quality and quantity, the calibre of a given mineral resource from initial inferred status through increasing levels of detailed exploration and expenditure to proven status primarily to attract and justify continuing investment in resource development before the start of extractive operations.

The main activity of geological assessment is field exploration including the mineralogical and chemical trace element analysis of samples collected from outcrops and/or drill cores (Fig. 2.4) showing the variation of quartz quality within the deposit. Drilling based on geological mapping and appropriate remote sensing techniques, determine the three dimensional extent of the mineralised body.



**Fig. 2.4** Aluminium distribution in the vertical drill core of a massive pegmatite quartz deposit, elevation in m

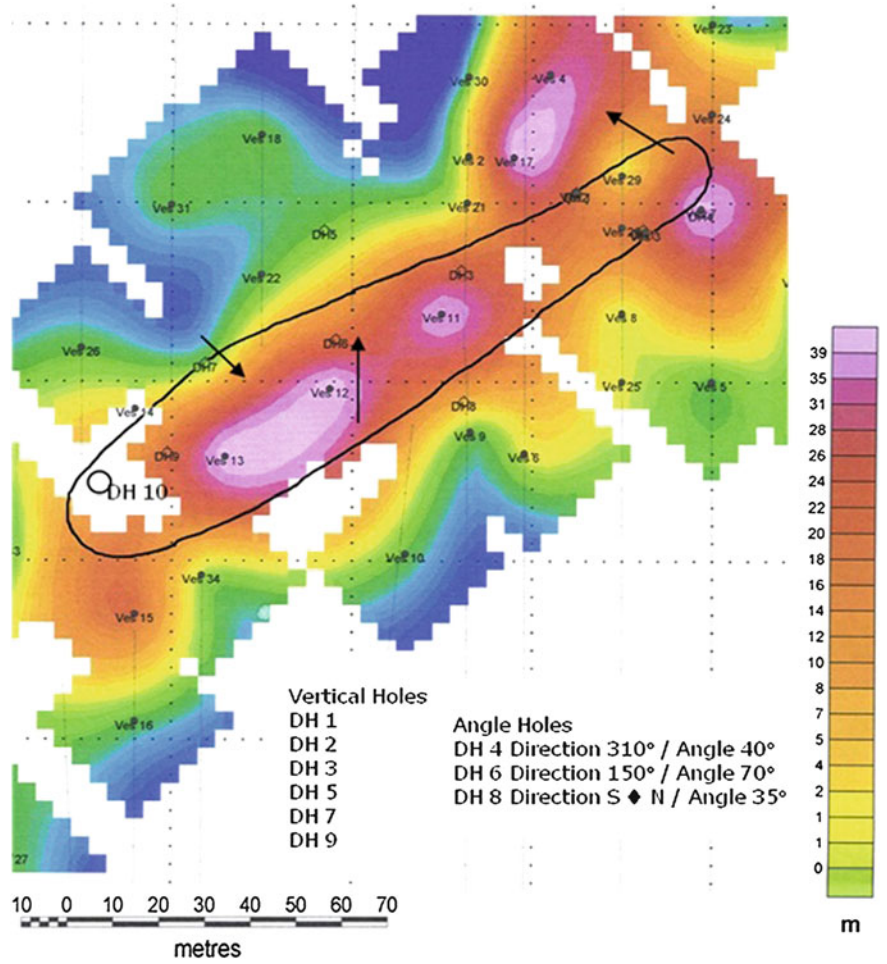
In order to reduce exploration costs information from initial drilling is combined with geophysical data derived from methods such as seismic, gravimetric, geoelectric or geomagnetic field surveys.

Geophysical resistivity profiles apparent lateral variations in resistivity of rocks using a specific electrode array over constant distances in specific locations. Vertical Electrical Sounding (VES) provides information on vertical variations in resistivity within a geological formation. Apparent resistivity values are correlated with the geological formations present to provide an interpretation of the extent of a deposit (Fig. 2.5). This assists efficient drill hole siting, the results of which ideally confirm and complement, in greater detail, resistivity data.

Once a quartz deposit has been identified the precise quality of its mineral content and potential for quality improvement are key factors in determining its economic value. Representative samples are taken for detailed investigation to evaluate the potential of the raw material to be processed into a high value refined product. Determinative mineralogical techniques characterise any fluid and/or mineral inclusions that need to be removed by applying tailor-made processes. The combination of mineralogical characterisation across the whole deposit by means of representative sample analysis with the identification of appropriate specific processes to remove impurities is crucial to the thorough evaluation of any raw quartz deposit for high purity and high value applications.

## 2.6 Analytics

Naturally occurring high purity quartz always has inclusions which are present either in the form of finely dispersed solids (mineral phases such as e.g. muscovite, rutile, calcite) or fluid (liquid and gaseous) inclusions which can provide valuable



**Fig. 2.5** Interpretation of lateral resistivity profiling and Vertical Electrical Sounding (VES) data presenting the thickness and subsurface distribution of a quartz body

insight into the conditions prevalent at the time of formation of the quartz. By the analysis of trace elements and impurities the conditions of formation of the quartz can be unraveled. Typically the bulk sample will be chemically characterized first. Then the size and distribution as well as chemical composition of the mineral and fluid inclusions are investigated in detail. The different steps in the analysis of raw quartz samples are discussed in the following.

### **2.6.1 Bulk Chemical Analysis**

Characterisation begins with bulk chemical analysis of representative samples of raw quartz. The results serve as a reference point for all processing tests in the later stages of the quartz assessment procedure. Special care needs to be taken at all stages of the analytical process:

- Contamination free comminution
- Acid digestion
- Trace element analysis by ICP-OES/MS or LA-ICP-MS

The technique most appropriate for detection of major chemical impurities is X-ray fluorescence (XRF), minor impurities down to the sub-ppm level are commonly detected by inductively-coupled-plasma optical emission spectrometry/mass-spectrometry (ICP-OES/MS) or laser-ablation ICP-MS. Laser ablation ICP-MS has the advantage, that the sample does not have to be digested, but has the disadvantage that a very small volume is probed, which is not representative of the bulk sample and may give misleading results.

Besides ICP-OES/MS there are complementary methods for the detection of trace elements in quartz such as electron spin resonance, cathodoluminescence, capillary ion analysis and gas chromatography (Götze et al. 2004). During initial characterization, typically 16 trace elements, defined to be most critical depending on the specific target application area, are usually determined:

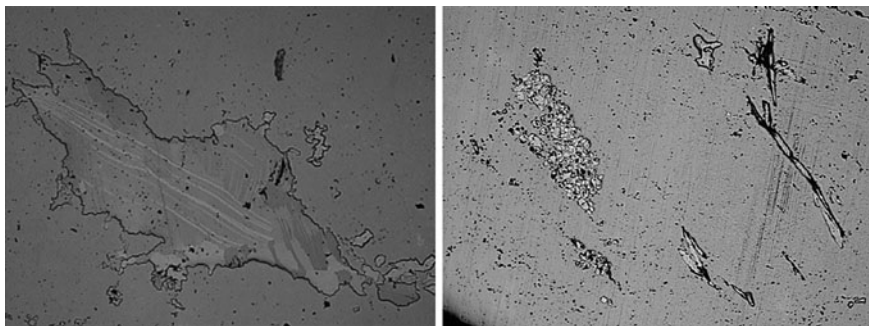
- Alkali metals, calcium and heavy metals—critical in lamp tubing and semiconductor applications
- Uranium and thorium—critical for microelectronics applications
- Boron and phosphorus—critical in solar silicon applications

Because of the low concentrations of trace elements multiple measurements and external standards such as specified and certified industry products (e.g. Iota Quartz) are required to ensure a very high level of confidence.

### **2.6.2 Characterization of Mineral Inclusions**

Although high purity is determined by the bulk composition, more information is needed to set up the most appropriate beneficiation route. Typical properties of raw quartz that must be characterized are:

- Size of inclusions
- Chemical composition of inclusions
- Spatial distribution of inclusions and localization of isomorphic substitutional elements (e.g. Al, Ti) in the quartz crystal lattice



**Fig. 2.6** *Left*: photomicrograph (reflected light) of a large xenomorphic calcite crystal with wavy deformation twins. Note also the presence of smaller irregularly shaped crystals nearby. Width of the picture is 600  $\mu\text{m}$ ; *Right*: photomicrograph (reflected light) of quartz with a cluster of apatite crystals on the *left* and tremolite fibres on the *right* side. Picture width is 2.3 mm

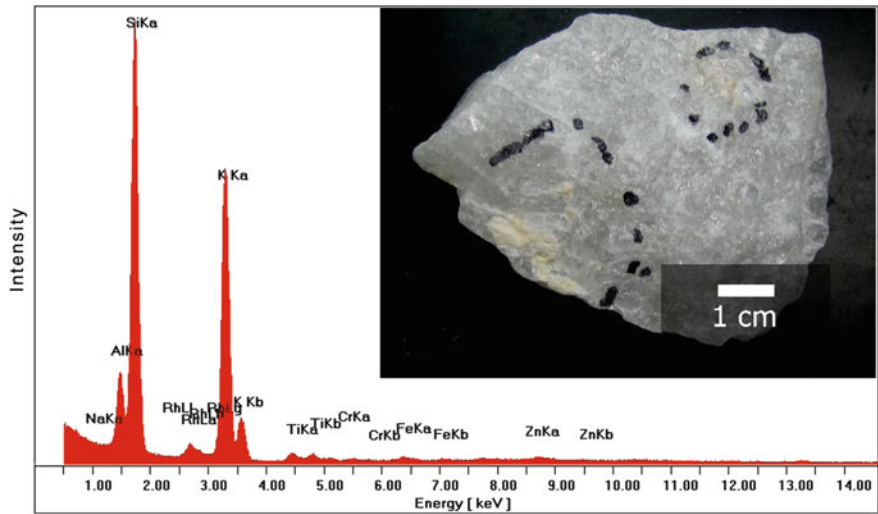
Optical microscopic analysis of raw quartz is the starting point. It allows rapid detection and a first overview of the sample texture and structure as well as impurities such as fluid and solid phase inclusions. An example of large xenomorphic calcite crystals with characteristic deformation twinning and apatite and tremolite inclusions determined by optical microscopy within the quartz matrix are shown in Fig. 2.6.

Impurities which are directly accessible to the analytics can most conveniently be detected by Micro X-ray fluorescence. An example of K-feldspar in quartz identified by Micro XRF is shown in Fig. 2.7. EPMA is another technique which is suitable for the precise identification of the chemical composition of minor inclusions such as K-feldspar in quartz shown in Fig. 2.8. Trace element contents ranging in the 100 ppm's can be detected by conventional EPMA. When improved background modeling, new quantitative “blank” correction routines and multiple spectrometers to improve the geometric efficiency are used, detection limits for Ti and Al as low as 2–3 ppm and 6–7 ppm can be achieved (Donovan et al. 2011).

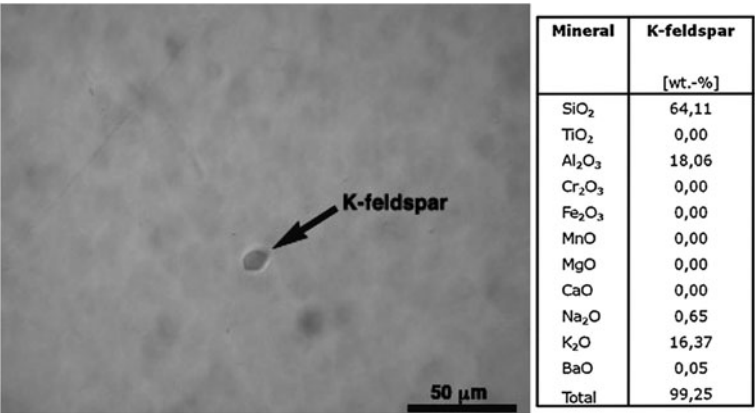
However, critical questions such as the localization of aluminium (isomorphic substitution for silicon in the quartz crystal lattice and/or mineral inclusions) can only be determined by combining optical microscopy with advanced spectroscopic methods (Tlili et al. 1989), e.g. Raman spectroscopy (Fig. 2.9), or electron paramagnetic resonance (EPR) spectroscopy. In Raman spectroscopy the sample is irradiated by laser light. A small part of the scattered light shows a shifted frequency with respect to the primary light resulting from inelastic scattering processes. From the resulting spectrum the oscillation frequency of the molecules can be determined.

To unambiguously identify if substitutional elements are incorporated into the quartz lattice structure electron paramagnetic resonance is used.

EPR is a method which is able to detect the presence of unpaired electrons in a material. The sample is placed in an external uniform magnetic field and irradiated by microwaves which interact with the unpaired electrons. In quartz unpaired electrons are present in the paramagnetic  $[\text{AlO}_4]^\circ$  centre or as electron- and hole centres which are caused by radiation (Götze and Plötze 1997; Nuttall and Weil



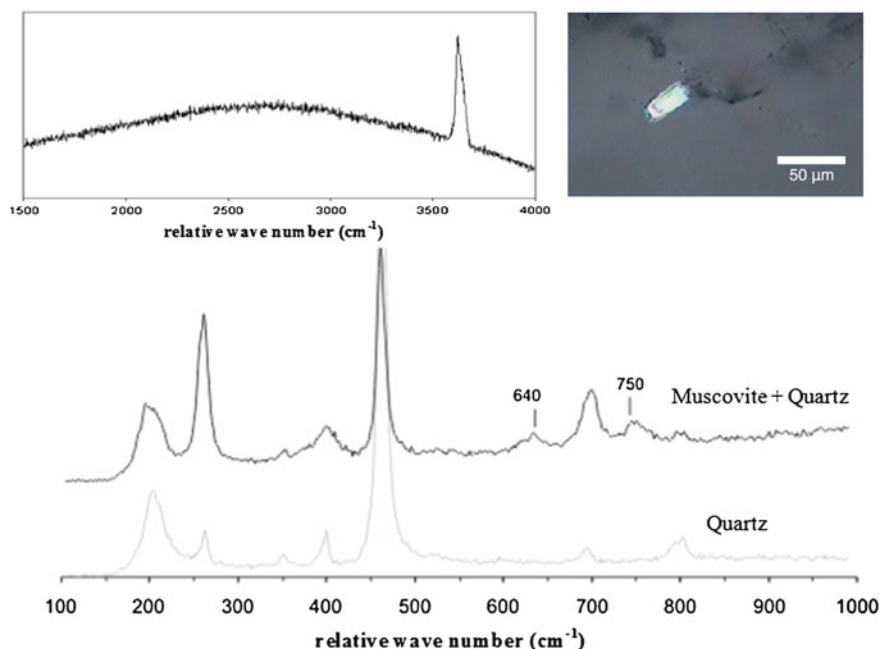
**Fig. 2.7** Photograph of K-feldspar in quartz (*whitish spots* in the area framed by *black ink dots*) and corresponding analysis by Micro XRF



**Fig. 2.8** Microphotograph (crossed polarizers) of a small grain of K-feldspar in quartz and corresponding results of electron probe microanalysis

1981; Okada et al. 1971). Figure 2.10 shows an example of EPR spectra of two quartz samples (labeled 1 and 2) from different deposits. In the upper part of the figure the simulated spectra of  $[AlO_4]^0$  and  $[TiO_4^-/Li^+]^0$  centers are shown. Measured spectra match those of the simulations and clearly confirm the presence of both types of centers in sample 1 (1a, 1b) and the presence of the former in sample 2. The aluminium contents in the samples, as determined by ICP-OES analyses, are 64 ppm and 10 ppm respectively.





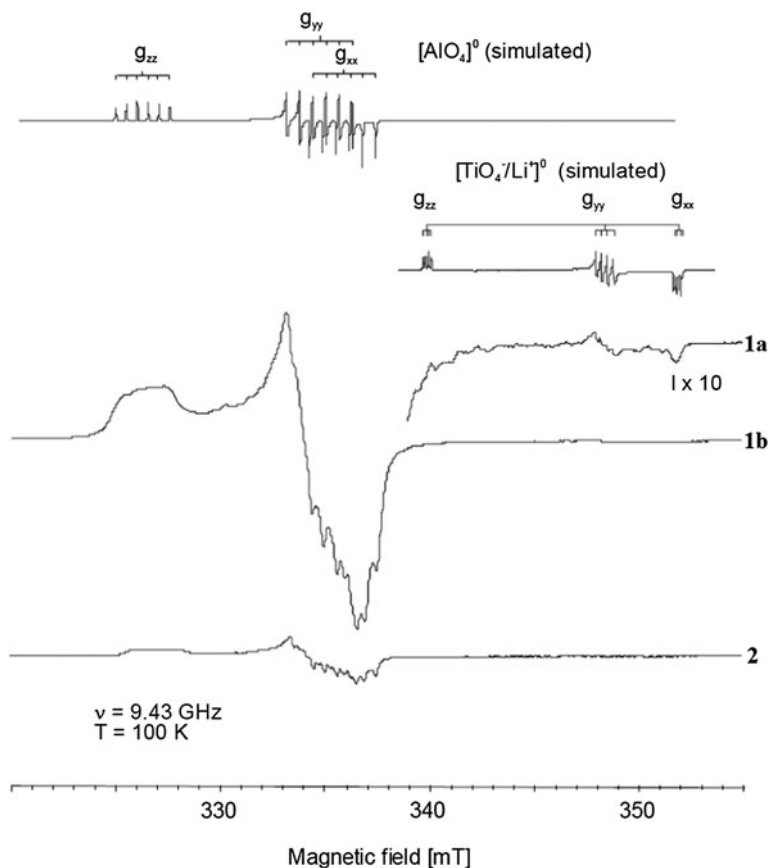
**Fig. 2.9** Laser micro-Raman spectra and photomicrograph (*inset upper right*) of a muscovite inclusion in host quartz (*grey*). Note the presence of the OH stretching peak at  $\sim 3630 \text{ cm}^{-1}$  (*inset upper left*) that is characteristic for aluminous micas (muscovite)

### 2.6.3 Analysis of Fluid (Liquid and Gaseous) Inclusions

Fluid inclusions are especially critical in relation to melting high purity quartz in glass making. Oftentimes, liquid inclusions are brines with elevated concentrations of alkalis which need to be removed to meet the chemical specification of the glass. In addition, gaseous inclusions may be critical with regard to quartz melting behavior. Quartz, when molten, is highly viscous and all gases which cannot escape or be dissolved will form bubbles leading to quality impairment in the final glass product.

Fluid inclusions are formed during the primary crystallization of quartz from cooling rock forming fluids and also as a result of secondary (re)-crystallisation processes related to tectonic events (Roedder 1984). They can be classified based on descriptive parameters like size, shape, color, refractive index, their origin (primary, secondary) and the number of physical phases (liquid (L), vapor (V), solid (S)) present within the inclusion (Van den Kerkhof and Hein 2001). An example of secondary fluid inclusions with aqueous two-phase liquid–vapor inclusions is shown in Fig. 2.11.

Oftentimes, high purity quartz contains different generations of fluid inclusions, which may contain gas and liquid, and sometimes even very small crystals.



**Fig. 2.10** Determination of substitutional elements Ti and Al in the quartz lattice by EPR; simulated EPR spectra of  $[\text{AlO}_4]^\circ$  and  $[\text{TiO}_4/\text{Li}^\circ]^\circ$  centers are shown in the top part; measured spectra of two different quartz samples (labeled 1 and 2) are shown below: sample 1 shows both the typical signature of  $[\text{TiO}_4/\text{Li}^\circ]^\circ$  and of  $[\text{AlO}_4]^\circ$  centers (spectra 1a, 1b), sample 2 indicates only the presence of a minor amount of  $[\text{AlO}_4]^\circ$  centers

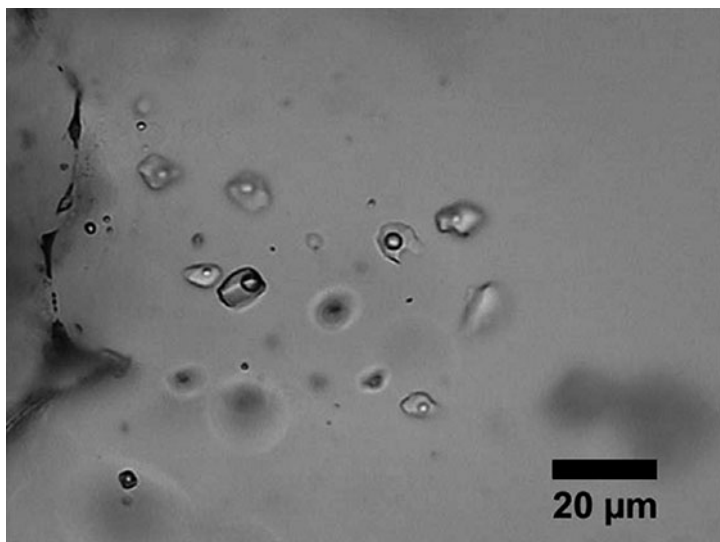
The microphotograph in Fig. 2.12 shows an example of such an inclusion of an opaque cross-shaped twinned crystal within the fluid inclusion.

Critical for process engineering can be:

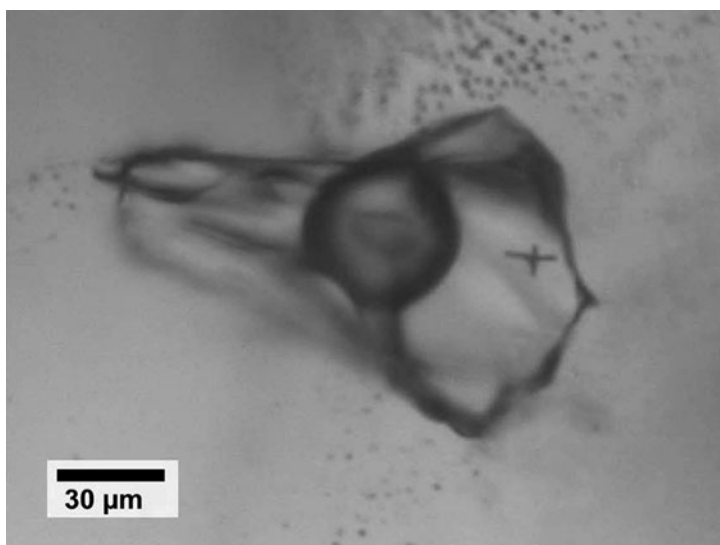
- Orientation of the fluid inclusions (along tracks or scattered)
- Chemical composition
- Pressure

The orientation of fluid inclusions is especially important since they may be aligned along tracks that will open during comminution or, if randomly scattered within the quartz crystals, their liberation by mechanical and physical processes will be prohibitively much more difficult. The chemical composition defines the





**Fig. 2.11** Secondary aqueous two-phase liquid–vapor inclusions with low degree of fill in quartz. Plane Polarized light



**Fig. 2.12** Microphotograph of a large re-equilibrated two liquid–vapor inclusion with a *cross-shaped black twinned crystal*. Plane polarized light

impurity level when element concentrations enriched in the fluid inclusions are forced in the silica glass during the melting process. Fluid inclusions may form bubbles making the silica glass less valuable. Since silica glass melt is highly viscous, smaller bubbles are not able to rise to the surface of the melt and so survive to unacceptably impair the quality of the silica glass.

In order to define the properties of the fluid inclusions, optical microscopy in combination with micro thermometry and Raman spectroscopy is employed. Specific options for process development, e.g. thermal treatment or opening of fluid inclusions by specific comminution technology, are explored according to the results of these analyses. Some quartz samples consist of clear and milky parts, the latter being richer in fluid inclusions than the former. The size of these parts is determined during the characterisation procedure in order to evaluate options for separating clear from milky quartz, by e.g. optical sorting. All these analyses are a full quality assessment that is a prerequisite for the design of optimum bench, pilot or technical scale processing tests.

## **2.7 High Purity Quartz Processing**

Conversion of raw quartz into refined high purity and high value quartz products needs advanced comminution technology. Comminution reduces raw quartz to the required product size and liberates mineral impurities. Further mechanical, physical, chemical and thermal steps are needed to separate or dissolve the impurities to meet final quality requirements. The main stages of the process may be summarised as

- Pre-processing (mechanical)
- Physical processing
- Chemical leaching
- Thermal treatment

### ***2.7.1 Pre-processing***

Based on the specific characteristics of the quartz deposit, one or more processing stages are required in order to liberate mineral impurities and fluid inclusions for further physical treatment:

- Initial crushing
- Optical sorting
- Comminution
- Classification to product particle size

Mined quartz lumps need to be washed to remove surface contaminations and crushed to produce granules in the centimetre size range. Crushing and grinding techniques need to consider both, to reduce the wear related

contamination of the quartz to a minimum and to selectively liberate the mineral inclusions. Electrodynamic comminution is an enhanced technology to liberate impurities in high purity quartz crystals. It minimizes the amount of undersize particles and contamination. Since crystal boundaries host most of the mineral impurities, downstream processing is more efficient and expected yield increases significantly compared with mechanical comminution techniques. This makes electrodynamic comminution one of the favored methods in high purity quartz processing.

Classification then provides closely defined size fractions beneficial for further processing. Recent developments have proven the effectiveness of optical sorting for the production of high purity quartz.

The technique separates the liberated components of raw materials on the basis of differing colour (or transparency) and shape, and may improve, or even replace, costly selective mining or hand sorting practices. Fully automated sensor based sorting devices can be equipped with color CCD-cameras, X-ray Transmission (XRT) and Near Infrared (NIR) technology for grain detection. After detection, non specified grains are selectively extracted from the bulk flow by a precise pulse of pressurized air from a high performance nozzle system. A specific benefit has been achieved for size fractions well below 40 mm, where manual sorting is not economical. Down to the 3–5 mm range, optical sorting is applied with high efficiency (Fig. 2.13).

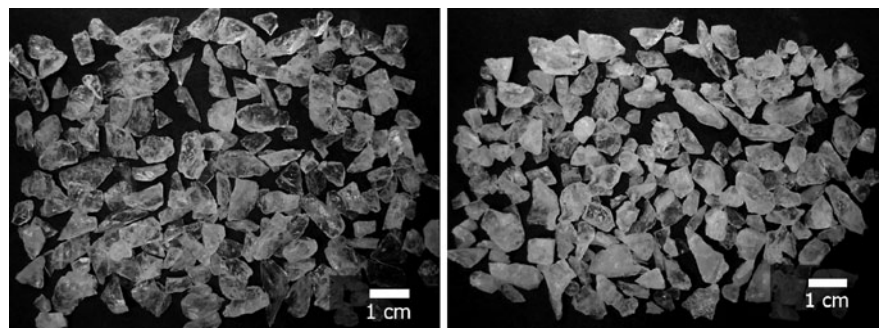
Optical sorting may be used to separate differently coloured quartz fractions such as patches of rose quartz, critical in solar applications owing to elevated phosphorus concentrations or smoky quartz with radiation induced discolorations. In addition clear quartz can be separated from milky quartz, being rich in fluid inclusions, and thereby often reduce the alkali content (Table 2.1) and improve the melting characteristics.

Standard size reduction and liberation of differing mineral constituents use jaw and cone crushers in order to reach the product grain sizes. However, these techniques introduce high amounts of contamination, owing to wear, especially into the fine product fractions. For high purity quartz alternative comminution techniques are applied:

- Autogenous grinding
- Electrodynamic fragmentation

In autogenous grinding the high purity quartz is ground on a bed of high purity quartz. By this comminution technology contamination from the wearing internal surfaces of the autogenous mill is minimised.

Electrodynamic fragmentation liberates quartz crystals in the composite rock largely without contamination and with low loss of undersize particles. A high-voltage discharge generates shock waves within the quartz lump causing it to fracture along grain boundaries (Andres et al. 1999; Dal Martello et al. 2011a, b). Since most of the mineral impurities are located along crystal boundaries downstream processing (e.g. chemical treatment) is more efficient. Yields increase significantly compared with mechanical comminution techniques. Moreover, this



**Fig. 2.13** Fraction 3–8 mm, clear quartz (*left*) and milky quartz (*right*) after optical sorting

**Table 2.1** Chemical characteristics of a quartz sample after optical sorting

	Al (ppm)	Fe (ppm)	Na (ppm)	K (ppm)	Li (ppm)	Ti (ppm)	Zr (ppm)
Quartz transparent	23	0.3	6.2	0.6	2.1	1.3	<0.1
Quartz milky	25	0.8	10	1.6	2.4	1.4	<0.1

**Table 2.2** Chemical analyses of quartz sample 0.1–0.3 mm after conventional comminution and electrodynamic fragmentation

	Al (ppm)	Fe (ppm)	Na (ppm)	K (ppm)	Li (ppm)	Ti (ppm)	Zr (ppm)
Quartz raw material	41	4.9	12	15	0.5	1.3	<0.1
Conventional comminution	23	464	10	3.5	0.6	1.9	<0.1
Electrodynamic fragmentation	28	1.3	13	4.7	0.6	0.5	<0.1

new technology is ideal for selective liberation of gas and liquid inclusion trails within the quartz crystals (Table 2.2).

**2.7.2 Physical Processing**

Impurities liberated during the preparation stage may be separated from quartz owing to their differing responses to physical processes, such as:

- Attrition
- Magnetic separation
- High tension separation
- Flotation

Attrition is applied to clean the surfaces of the quartz particles. Thereby fine particles attached to quartz surfaces, e.g. clay minerals or iron oxide coatings, are either washed away or liberated for their subsequent physical separation. Magnetic separation removes heavy minerals from quartz as they are mostly paramagnetic or ferromagnetic. These minerals are attracted by a magnetic field. Quartz, being diamagnetic, is repelled. Since magnetic susceptibility is strong in the case of ferromagnetic minerals only moderate magnetic field strengths are necessary for their separation, whereas higher field strengths are required to separate paramagnetic minerals.

High tension techniques separate minerals owing to differences in their surface conductance. For this processing step particles are uniformly passed through an electrostatic field. The electrostatic separator consists of a heated chamber where the electrodes are situated. The generated electrostatic field is up to 120 kV. Feed material is activated by heating the sample or by the addition of diluted acids to the feed material prior to heating. Typically, feldspar impurities may be separated from quartz via high tension as a dry alternative to froth flotation.

Froth flotation selectively separates minerals according to differences in their ability to be wetted, enhanced or suppressed by conditioning reagents. Separation takes place in a water-filled medium into which the ore is fed to form a suspension which is agitated to avoid sedimentation processes. A frothing agent is added and air introduced to form rising air bubbles. Hydrophobic/Hydrophobized mineral particles (such as heavy minerals, feldspar or mica) attach to the air bubbles and rise to the surface forming froth whereas hydrophilic (wetted) particles remain below the froth layer in the suspension. The mineral-carrying froth is removed.

Flotation process designs vary in complexity depending primarily on the type of mineral, degree of liberation, and the desired purity of the product.

### ***2.7.3 Chemical Treatment***

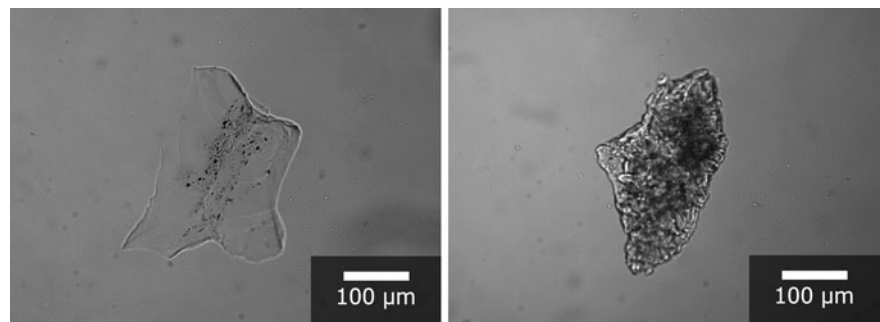
Chemical treatment is an important addition to physical processing methods in order to achieve maximum purity quartz through the removal of surface impurities. Acid washing, leaching and hot chlorination are the three chemical treatment processes.

While acid washing uses less aggressive acids such as hydrochloric or sulphuric acid, leaching uses an advanced hydrofluoric acid process at elevated temperatures, to remove liberated surface impurities most effectively. In addition, those impurities enriched in micro fissures and along dislocations, will be liberated and removed owing to an enhanced dissolution rate of quartz in regions where impurities are concentrated.

In the hot chlorination process, quartz is heated to temperatures of 1,000–1,200°C in a chlorine or hydrogen chloride gas atmosphere. This refining process is suitable to specifically reduce the level of alkali metal impurities

**Table 2.3** Chemical analyses of quartz sample 0.1–0.3 mm after chemical treatment

	Al (ppm)	Fe (ppm)	Na (ppm)	K (ppm)	Li (ppm)	Ti (ppm)	Zr (ppm)
Quartz after magnetic separation	21	0.2	3.1	1.0	2.2	1.2	<0.1
Acid washing	21	<0.1	2.8	0.9	2.2	1.2	<0.1
Leaching	20	<0.1	0.7	0.3	2.2	1.2	<0.1
Hot chlorination	21	<0.1	0.2	<0.1	1.6	1.1	<0.1



**Fig. 2.14** Comparison of quartz grains of raw quartz, fraction 0.1–0.3 mm (*left*) and quartz after thermal treatment (*right*)

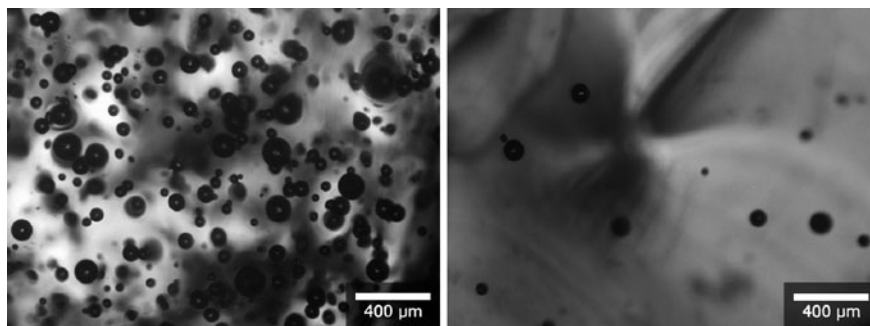
(Table 2.3) which are highly restricted in lamp tubing and semiconductor applications.

**2.7.4 Thermal Treatment**

Thermal treatment (calcination) of high purity quartz improves its melting behaviour owing to the removal of fluid inclusions (Fig. 2.14). Depending on the degree of filling, the pressure and applied calcination technology (atmosphere, temperature etc.) a significant reduction of the bubble content in the silica glass has been observed (Fig. 2.15).

**2.8 Conclusion**

Whilst many industrial minerals deploy off-the-shelf technology solutions most speciality minerals require tailored processes and specially designed equipment that cannot be conceived prior to thorough analytical evaluation. That is why detailed investigations of the specific impurities ubiquitously found in quartz need to be performed before tailor-made processing concepts may be aligned with realistic



**Fig. 2.15** Comparison of melting results of raw quartz, fraction 0.1–0.3 mm (*left*) and quartz after thermal treatment (*right*)

investment costs and quality requirements. Engineering services need to cover all the technology and economic details such as estimation of investment costs, details of main plant and equipment, calculation of mass balances, energy requirements, and specific production costs before the final investment decision can be made. A precise and sustainable definition of the product split, in terms of relevant chemistry and appropriate physical characteristics, and end-user acceptance are two prerequisites for the success of any minerals-based project. End-user approval of processed samples at potential qualities is the ultimate, and necessary, risk management process.

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