A REVIEW OF PREVIOUS WORK ON IMPORTANT PROPERTIES OF QUARTZ FOR FESI AND SI METAL PRODUCTION

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ABSTRACT

Quartz is one of the main raw materials for the carbothermic production of ferrosilicon and silicon metal. The ideal process is written:

$$SiO_2 + 2C = Si + 2CO$$

The real process is much more complicated, depending on the quality of the raw materials. Several research projects have been carried out on quartz for the (Fe)Si process during the last 50-60 years.

One of the important properties that have been discussed in this review is the volume expansion that takes place between 850 °C to 1000 °C and explosive disintegration for some quartz types. No final and definite conclusions have been made but several reasons have been mentioned: The influence of the phase transformation to tridymite, which takes place within the same temperature interval, has been discussed in several papers. Alkali impurities have been mentioned as a critical factor for this transformation to take place. Other researchers have mentioned mica impurities as a critical factor for the behavior of the quartz at these temperatures. Studies of fluid inclusions in quartz was reported in some papers focusing on the volume expansion of these during heating as a source of explosive disintegration, especially along planes of healed micro fractures that often contain vast numbers of such inclusions.

Several methods for investigations of the important properties of quartz have been presented and these provide a good basis for the further research on quartz raw materials.

1. INTRODUCTION

Many of today's advanced materials depend on quartz as a raw material. Either as processed quartz or as silicon metal produced from quartz. Examples of such advanced materials are the computer chips that are used in all kinds of electronic equipment such as computers, mobile phones, refrigerators, etc., which all use silicon and quartz as raw material. Another important consumer of silicon metal is the photovoltaic industry that is growing fast. The silicon demand from the solar cell industry is rising and the challenge of the shortage of silicon with the right price and purity is already here. Silicon metal is also used as a raw material for the chemical industry in e.g. silicones. Ferrosilicon is used in steel making for desoxidation and alloying.

Silicon is produced industrially by reduction of silicon dioxide with carbon in an electric arc furnace at temperatures higher than 2000 ºC in the hottest parts, by a reaction that can be written ideally as:

$$SiO_2 + 2C = Si + 2CO \quad (1)$$

Quartz and quartzite are the source for Si in the carbothermic process for ferrosilicon and silicon metal ((Fe)Si). The industry has defined a list of absolute requirements to the raw material that must be achieved in order for the process to be optimized e.g. Schei et al. [1]:

– Chemistry (trace element content, e.g. Al, Ti, B, P, Fe, Ca))
– -Lump size (typical 10 – 150 mm)
– -Mechanical strength
– -Thermal strength
– -Softening properties

This review will focus on the work carried out with respect to the thermal strength of the quartz. This is important for the behavior of the quartz inside the furnace. Especially for how the quartz reacts to the sudden rise in temperature when it is fed to the furnace. If the heat makes the quartz disintegrate, the resulting fine-grained particles will create problems for the gas flow inside the furnace.

The quality of the raw materials is important for the quality of the final products from the (Fe)Si furnace. The industry has so far been most concerned about the quality of the black (carbon) raw materials. Consequently, research on the quartz raw materials has had low priority. However, several smaller and larger projects have been carried out with respect to the quartz raw materials during the last fifty years. Most of the available literature comes from projects carried out in Norway. There may be many reasons for this, but the major reason is that Norway has been the world's leading producer of FeSi and Si metal. This will of course be reflected in the available research material. Another factor is the secrecy around the process that can be seen within the industry. When one company has found a way of improving the process, this is kept as an industrial secret in order to achieve a competitive advantage. Therefore, the following review is based only on literature that has been published, or has recently been made public by the industry.

Knowledge about the raw materials becomes more important when the requirements to product quality increase. Therefore, an overview of the knowledgebase of characterization methods and results is important.

2. WORK ON QUARTZ FOR SI-METAL

2.1 Work up to the mid 1960's

According to Geiss [2], the Norwegian FeSi producers started to show interest in the cause of the behavior of the quartz/quartzites in the furnace towards the end of the 1950's. It has been difficult to find literature on the earliest work mentioned, thus only descriptions provided by Geiss [2] are available. During the late 1950's industrial tests were carried out by "Electrochemical Research Station" at Fiskaa on different Norwegian quartz and quartzite. These samples were heated to 1250 °C; and after heating, changes in the density of the samples were recorded. The conclusion of these investigations, based on the changes in density, was that some of the quartz had been transformed to tridymite. However, according to Geiss, later investigations on different quartz types made modifications of the conclusion necessary.

Geiss [2] also refers to T. Nervik, who studied the transition from quartz to cristobalite and its influence on the thermal strength of the material. Quartz, cristobalite and a glass phase were separated and identified by differential thermal analysis (DTA) and buoyancy in liquid (the type of liquid is not specified). According to Geiss, these results only exist as a manuscript and the work seems to have never been finished. Thus, the only conclusion available from this work is that different pegmatite quartz samples were weakened by the α- (low)/ β- (high-) quartz phase transformation. The fact that the heating weakens different types of quartz has been confirmed in later work. However, different authors give different answers to this effect, and Nervik is the only who blames the α- / β-quartz phase transformation for all the effects. Later work, as will be shown in another section, uses more combined investigations and sees things in another perspective. Nervik would perhaps have given more specified arguments if the manuscript had been completed.

2.2 Work from the late 1960's to mid 1970's

In the 1960's and through the 1970's there were several Norwegian projects related to the problems with quartz raw materials. Many of these small projects showed some interesting conclusions based on the continuation of other work. It is not clear, if the different research groups knew about each other's work or if the projects were completely independent. However, the conclusions overlap to a certain degree and give new

answers to some questions. These reports have not been found, so these comments are, as for the previous paragraphs, based on the report from Geiss [2].

During the 1960's, a group of researchers at the Norwegian Geological Survey (NGU) worked on the significance of the defects on the thermal decrepitation of natural quartz. According to Birkeland and Carstens [3], this was a result of several meetings between NGU, "Metallurgical committee" and "Norwegian Ferrosilicon Producers' Central Committee". As a result of these meetings, NGU found this work to be its responsibility. The report presents three parts where the first part considers thin-section investigation of quartzites before and after heating. Three samples of each quartzite were cut into 1x5x5 cm. Two of these were heated in a furnace to 1000 ºC with different heating rates: One sample was introduced to the furnace at room temperature and heated to 1000 ºC over a period of 20 min, while the other sample was introduced directly to the furnace at 1000 ºC. Both samples were slowly cooled (2-3 hours), however, there are no specifications of how long the samples were kept at 1000 ºC. The third sample was used as an unheated reference. The three samples were then prepared as polished thin sections and studied by optical microscopy. Some interesting observations were made: The authors were surprised that the traces of fluid inclusions did not seem to be important for the fracturing of the sample. Deformation structures like undulate extinction, sub-grain segmentation, deformation lamellae and deformation bands, and most of the inclusion planes, seem unaffected by the heating. Birkeland and Carstens [3] observed that the heated rocks were more fractured than the unheated rocks and there were indications that the cracks tend to pass through each single grain. The fracturing was interpreted to be non-qualitative. The fractures were of the same type and distribution as in the fresh rocks. Birkeland and Carstens [3] also discussed the outcome from potential similar tests on smaller samples and concluded that such samples would probably show more and different fracturing. They also discussed the outcome of heating the samples to different temperatures and thought that different temperatures would give different results.

Part two presents microscopy of quartzites and single-crystal quartz in a heating stage microscope. The samples were prepared as 1 mm thick and 6 mm diameter cylindrical slices, polished on both sides. The apparatus used was a Leitz 1350 heating stage mounted on a Leitz Ortholux transmitted light microscope. The heating occurred over five to ten minutes up to 1300 ºC. The heating was carried out stepwise in order to lower the heating rate. This gave, according to Birkeland and Carstens [3], an irregular heating rate. Results were recorded as visual observations of differences in the temperatures when cracking occurred during heating. In most samples, cracking appears at 300 °C – 400 ºC. This seems to be related to fluid inclusions and sometimes to grain boundaries. The cracking seems to increase in most of the samples towards the transition from α-quartz to β-quartz at 573 ºC. After 600 ºC usually nothing happens and the samples show some sort of relaxation of the samples up to 900 ºC. Above 900 – 1000 ºC, there is regenerated activity in several samples. The authors describe the activity as explosions that destroy the samples. Birkeland and Carstens conclude that this type of explosion is of importance for the strength of the quartzite. However, there is no discussion around the difference between the small sample size used in the investigations compared to the larger material sizes used in the actual process.

This study is advanced to a degree that even today's technology seems to have stalled on this level. The heating stage investigation presents some interesting observations, although these are based only on visual observation and are difficult to quantify. Today's technology is more advanced in the way that images can be captured sequentially (or even recorded on digital video) such that the observations can be better illustrated.

The third part of the report consists of comments to numerous specialty investigations. One of the techniques mentioned here is the so-called decreptiograph or better known as thermosonimetry (TS) of minerals. The equipment has not been used in this project but the theory around it is briefly described. It is mentioned that the project initiated the construction of one such decreptiograph at the Dept. of Physics at the Norwegian School of Technology (NTH, now the Norwegian University of Science and Technology (NTNU)). This equipment has later been described and tests carried out by Lønvik [4-6] and Lønvik and Smykatz-Kloss [7] among others.

Lønvik [4, 5] investigated different types of quartz by thermosonimetry. Samples of the rock were made by drilling cylindrical cores with approximately 8-12 mm diameter (varying) and around 3 - 4 grams. These sam-

ples were then analyzed in a chamber capable of heating to ca 1000 °C and a stethoscope mounted in the sample chamber recorded the acoustic effects from the sample during heating. Lønvik [4, 5] proved that the equipment was capable of measuring the acoustic effects, and the intensity of these, created in the samples during heating.

Peaks at 550 °C to 580 °C represent the phase transformation from α- to β-quartz. Peaks also occurred at 870 °C and 960 °C that were interpreted as representing the quartz – tridymite transformation. These peaks were not present in all the samples, indicating that tridymite transformation is present in only some of the samples.

2.3 Work during the late 1970's

Lønvik also carried out investigations reported by Geiss [2] on two samples from that project. These results gave the same conclusion as the earlier TS investigations mentioned above. However, Geiss mentioned an important drawback: This method is only capable of heating samples to 1000 °C, which is too low to confirm the effects of heating described by others e.g. [3] at temperatures higher than 1000 °C. Thus, he argued that dilatometry is more useful because it has a higher temperature range, and can be handled more quantitatively.

In a letter to various people, Birkeland [8] summarized some of the work he carried out at the Norwegian Geological Survey (described by e.g. Birkeland and Carstens [3]). He also made comments on work carried out by the Metal Properties Group at Niagara Falls (reference not available) which concluded that "cracking is caused by and correlated to the amount of optical visible mica (at 10x magnification) and $Fe(OH)_3$". Birkeland disagreed with these conclusions based on the fact that high amounts of mica are observable only if the quartzite is coarse-grained and of relatively high metamorphic state. The coarse-grained fabric and high metamorphic state were also thought to be a reason for low thermal stability, such that no conclusions can be drawn to the mica itself. He also referred to his own work with the Kragerø quartzite [3] that had no visible mica or $Fe(OH)_3$, but still disintegrated heavily when heated to 1000 – 1100 °C. At the end, Birkeland concluded that one has to distinguish between different types of cracking. Birkeland believed that cracking could be both "dangerous" and "unimportant". He probably related this to the observation of large grains (flakes) of mica, which will create cracking along its boundaries with certain effects as described by Mrs. Faulring (Birkeland gives no reference but she probably belongs to the Niagara Falls group). Birkeland questioned if these effects are dangerous.

Geiss [2] presented a high temperature investigation of quartzite from the Gudvangen deposit, Kragerø, Norway. This is a comprehensive report with considerations made around the different methods used and the comparisons between different types of equipment for each of the methods. Geiss considered such as regular optical microscopy and fluid inclusion studies as well as more advanced techniques such as differential thermal analysis (DTA), TS, dilatometry, high-temperature XRD and softening point measurements (by use of compressive strength measurements).

Optical microscopy showed that the samples were coarse crystalline, completely recrystallized quartzites that had undergone plastic deformation. Numerous fractures were healed and the samples contained three generations of fluid inclusions. The rocks looked very similar and they could not be easily separated into "good" and "bad" quartz based on microscopy itself.

The DTA analysis was carried out on three different types of equipment (own equipment, by Birkeland and test analysis by two instrument manufacturers). Birkeland carried out the most extensive investigations with regards to the amount of samples, while the other equipment were tested on two of these samples. Geiss [2] showed that the equipment gave more or less the same results when the analyses were carried out with the same heating rate and paper speed (the paper speed determined the resolution of the results). He also stated that reanalyzing already heated samples might give interesting additional information, especially about the generation of cristobalite (and Tridymite) from the initial analysis. Geiss also concluded that Al_2O_3 should be used as standard. The analysis carried out by Birkeland showed, except for the α- to β-quartz phase transfor-

mation, zero to one peaks for "good" quartz and one to several peaks for "bad" quartz. This may be interpreted as a criterion for distinguishing "good" and "bad" quartz samples.

Dilatometry analysis was also carried out in the project reported by Geiss [2]. These were as the DTA, carried out on three different dilatometry equipment. Geiss [2] concluded that the best results were obtained by using relatively coarse and compressed diagrams and summarized the results to say that "good" quartz shows little or no effect between 800 °C – 965 °C and "bad" quartz shows strong effects in the same interval. Geiss [2] related this to the generation of tridymite and said that the effects between 800 °C and 965°C increased at alkali content above 0.15%. However, he made this as an assumption and stated that the generation of tridymite had not yet been proved. This has to be done by using, for instance, XRD or optical microscopy of thin sections. Still, he concluded that the content of alkalis seem to have a crucial influence on the fracturing of the rock during heating.

The softening point of quartz was measured using "standard" equipment at SINTEF Metallurgy. Samples from each piece of quartz were made as cylinders with diameter 31.6 mm and height 31 mm. The cylinders were exposed to a load of 2 kp/cm^2 and the temperature was recorded at 0.6 % and at 40 % compression of the samples (for complete method description, see e.g. Seltveit [9]). The analyses showed that the softening interval were as narrow as 10 °C. The chemical analyses with respect to Na2O were extremely high in some of the samples, up to ten times the value in average samples. Visual observations of changes (fracturing and dark spots) were made as well. The conclusion from this work stated that there were no significant differences between the different quartz samples. The reason Geiss [2] carried out these investigations was that this was the only method capable of giving results up to the smelting point of quartz.

In an oral communication with Geiss [2], Birkeland described x-ray diffraction (XRD) on quartz samples that initially were heated (temperature and other vital details were not reported) and further cooled and crushed. According to Geiss [2], Birkeland reported that only high-quartz was detected. These analyses were carried out on pulverized rock. Geiss' [2] hypothesis was that the crushing alters the lattice tension and thus leads to different reactions to the heating. He believed this was the reason that only quartz was found and no tridymite, as were interpreted to be the cause of fracturing in other tests. In order to check this hypothesis, Geiss [2] carried out high-temperature XRD analyses on larger pieces of quartz. Samples were sent to three different laboratories. He concluded that all of the analyses were more or less unsuccessful and did not confirm the possible generation of tridymite in the most alkali rich samples that were seen from the dilatometry investigations. Tridymite (and cristobalite) were found only in samples heated to 1200 °C and higher. Samples cooled to 80 °C showed cristobalite, tridymite, and only weak deflection for quartz. Analysis of the same samples after crushing showed quartz, cristobalite and possibly tridymite. According to Geiss [2], the absence of tridymite in the samples after crushing was caused by the crushing, which seemed to alter the SiO_2 lattice. He concluded that as long as the samples had not been accidentally switched, the generation of tridymite could not be the reason for the heavy fracturing seen between 800 and 965 °C in dilatometry investigations (e.g. Geiss [2]). Geiss wrote that he intended to do more of these investigations and even described the procedure he was planning. However, no reference has been found to these further investigations.

2.4 Work during the 1980's

Seki et al. [10] discussed the influence of raw materials on the production of 75% ferrosilicon. The paper considered the influence of all raw materials and referred to observations of a furnace and investigations made during excavation of a furnace. These investigations gave interesting observations and statements for the requirements to the quartz raw materials but the only test method mentioned was the Seger Cone test (cone test for refractoriness). This test were carried out on the considered raw materials but the theory and methodology were not discussed in the paper (see e.g. Seltveit [9] for method description). This is the only reference to the use of this method on this type of material that has been found. However, according to Kallfelz [11] this is an interesting method for testing the softening properties of quartz and can possibly be compared with results from dilatometry.

Malvik and Vokes [12] summarized research on the liberation of minerals by comminution. This research was concentrated on Norwegian raw materials for the metallurgical industry with emphasis on dolomite. However, quartzite was also tested to certain degree. Image analysis was carried out to determine the form factor and cohesion factor of the rock. The Norwegian Tana quartzite (regarded as having good thermal properties) and the Finnish Nilsiia quartzite (bad thermal properties) were investigated. The results show that even if the form factors are almost identical, the cohesion factors can be used. The Tana quartzite had a much better cohesion factor than the Nilsiia quartzite along the grain boundaries. Thus, this may explain the differences in thermal stability.

Lønvik and Smykatz-Kloss [7] compared the DTA and the TS techniques. The results confirmed the agreement of the main features of TS to those of DTA. They emphasized the higher resolution of TS in case of overlapping effects compared to DTA analysis.

Malvik [13] discussed earlier quartz investigations and listed possible parameters that influence the thermal properties of the quartz. These parameters are listed in Table 1.

Table 1: Parameters influencing the thermal properties of quartz (after Malvik, 1986a)

A	Internal parameters in quartz	Grain structure	Size
			Shape
			State of recrystallisation
			Grain bonding
		Fluid Inclusion	Amount
			Type
			Composition
		Chemistry	Foreign ions
			Trace elements
		Strain conditions	
		Elasticity module	
		Crystal structure	
B	Effect related to foreign minerals	Type of minerals	Mica most important
		Amount of minerals	
		Grain-size	grain size distribution
		Composition of other minerals	
C	Effect of the total chemistry	Diffusion of elements into quartz	Negative influence

Malvik [13] emphasized the fact that the TS technique had been further developed to be capable of heating to 1650 °C, something that gave the method a higher capacity, especially as the higher temperature enables the TS technique to detect acoustics in the entire interval that also is covered by dilatometry.

Malvik [13] reported investigation methods that he proposed for different types of quartz to see what causes the deflection between 850 and 1000 °C. As he interpreted the results, this is caused by mica impurities and/or tridymite formation catalyzed by high content of impurities. The types of quartz to be investigated were also specified: Malvik [13] proposed a limited selection of bad thermal quartzes and a reference sample of good thermal quartz.

Malvik [14] performed further investigations on the role of mica on the thermal properties of quartzite. This was carried out on two of the quartz samples used by Geiss [2] and two other samples. Malvik carried out additional dilatometry on one sample (the others were already analyzed by Geiss [2]) and TS on all the samples. TS was carried out on different types of prepared samples: powder of unsorted samples, on samples consisting of mica separated from the rock and the quartz resulting from the extraction of mica. In addition, analyses were carried out on different grain size fractions of the crushed material. Malvik [14] concluded that the mica is the cause of the large effects seen in dilatometry and TS, thus mica plays an important role for the thermal stability of the quartzite. However, Malvik [14] made reservations to the type and occurrence of the

mica. Thus, he disagreed with the critical comments made by Birkeland [8] on the conclusions made by the research group at Niagara Falls.

Lønvik [6] discussed the theory around the TS technique. He presented data around the phase transformation from high-quartz to high-cristobalite. Constant firing time at 1470 °C for one hour prior to the investigations showed that quartz of different origins were transformed to cristobalite with different transformation rates. Thus, he concluded that the grain size and the presence of impurities influence the transformation rate.

Martinsen [15] studied the fluid inclusions in different quartzes and compared these with regard to the classification of the quartz as having "good" or "bad" thermal properties. Martinsen observed only secondary fluid inclusions in most samples except one quartzite that contained pseudo secondary inclusions. By plotting the data collected in a diagram (see Martinsen [15] fig. 8) as homogenization temperature vs. salinity, the two types of quartz regarded as having very good thermal properties, plot together. Martinsen concluded that the amount of samples and data in his investigation was too limited to give a final answer, but that it was reasonable that the fluid inclusion composition in the quartz could say something about its quality as a raw material for the (Fe)Si process. This seems to have been a more advanced fluid inclusion study than the one by Birkeland [2]. Birkeland studied only the shape and visual content of the inclusions by ordinary optical microscopy, while Martinsen [15] used a freezing and heating stage to study smelting temperatures (water and solid phases) and the homogenization temperature for the inclusions. Thus, Martinsen could say more about the properties of the fluid inclusions than Birkeland. Fluid inclusion studies on quartz for the glass industry have been reported by e.g. Gemeinert et al. [16]. He demonstrated that the properties of the fluid inclusions determine the behavior of the raw material during phase transformation and smelting process. The conclusion states that low-hydrothermal samples of quartz show high speed of phase transformation from β-quartz to β-cristobalite, which causes a release of the inclusion contents. This is regarded as positive for the production of silica glass, in order to avoid gas bubbles in the glass. These observations can also be relevant for quartz for the (Fe)Si industry. It certainly indicates that fluid inclusion is important for the cristobalite formation and, thus, also for the heating rate of the material.

Malvik [17] discussed the relationship between mineralogical texture and comminution characteristics for rocks and ores. He used several case examples and one of these was the grain structure of quartzite. Malvik investigated two quartzites of different thermo mechanical properties: The Tana quartzite ("good") and the Nilsiia quartzite ("bad"). Investigations were carried out using a technique developed by Boasen and Fjerdingstad [18], combining backscattered electrons (BSE) and cathodoluminescence (CL) images, to give an indication of the cohesion between the different quartz grains. These results were also discussed by Malvik [19]. Quartzites that are of low recrystallization and low metamorphic grade show differences in luminescence brightness in the different generations of quartz. The silica cement and the recrystallized quartz will have less luminescence than the low luminescence recrystallized quartz. In completely recrystallized quartzites, there will be no contrast between different quartz grains. The author concluded that it is important that the ratio cement/clastic materials is highest possible if one wants to avoid the collapse of the grain structure when heating the quartzite. The discussion around CL as a method for characterizing quartzite raw materials was continued in a paper presented by Malvik and Lund [20]. This paper defines problems involved with quartzite as a raw material for (Fe)Si metal production. In this report, the authors describe several test methods that can be used in the field when searching for new deposits, and further in the process of testing possible methods. Most of these methods have been described earlier, such as CL (e.g.[17, 19]), Dilatometry (e.g. [2]) and TS (e.g. [4-6] and [7]).

2.5 Recent work on quartz

During the 1990's several people within Elkem ASA Silicon Division have been engaged in work on quartz raw material. Unfortunately, most of this work exists either as confidential reports or as memos (e.g. [21]).

At NTNU, two different quartz related projects have been carried out during recent years: At the Department of Geology and Minerals Resources Engineering, professors, post docs and PhD-candidates have been engaged in the project "The value chain from mineral deposit to beneficiated product with emphasis on

quartz". This is a Strategic University Program (SUP) and is being carried out in cooperation with e.g. NGU, Elkem ASA Silicon Division and several other industrial partners. At the Dept. of Materials Technology, researchers have been engaged in another SUP project: the project "From sand to solar cells".

Researchers at NGU have been working during many years on the exploration and investigation of possible quartz deposits in Norway. However, none of these projects has discussed the thermal properties of quartz for the ferrosilicon and silicon metal process.

3. CONCLUSION

The research activities carried out on the thermal properties of quartz and quartzite raw materials for the metallurgical production of ferrosilicon and silicon metal during the last five decades is numerous. Most of the literature that was found is from research carried out in Norway, both published and unpublished. A possible reason for this is that Norway has been the leading producer of ferrosilicon and silicon metal, combined with the confidentiality policy connected to the research carried out in the industry.

This review shows that much of the discussion about "good" and "bad" quartz has been related to the explosive disintegration of some quartz types at 850 to 1000 °C. The different reasons discussed are the generation of tridymite and the alkali impurities that must be joining this phase transformation as well as the influence of mica on the thermal stability of the quartz.

The correlation between Al_2O_3 and/or K_2O content with observations in dilatometry indicates that mica is present in samples which show critical deflection in the interval between 850 and 1000 ºC.

Many of the papers discussed in this review are related to the properties of quartzites. However, pegmatitic and hydrothermal quartzes that show low thermal stability, but the mica is probably not the reason here.

Fluid inclusions in quartz are also a possible factor that influence the thermal properties of quartz and this should be studied in more detail. Although several researchers have investigated fluid inclusions, only Martinsen [15] has looked at the composition of these inclusions. Further investigations should continue this study and look at the fluid inclusions related to the formation and later alteration of the quartz.

It seems clear that no final conclusion has been made with regard to the parameters influencing the thermal properties. The investigations discussed in this paper consist of a vast collection of advanced techniques. They certainly form a basis for further investigations.

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