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ANNEALING STABILITY OF CRISTOBALITE NANO CRYSTAL IN BRAVAIS CRYSTAL LATTICE AND BIOCHEMICAL HEALTH HAZARDS OF SILICA

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ABSTRACT

Nanocrystalline powder of SiO_2 synthesized by gas phase condensation technique has been characterized by X-ray and electron diffractometric techniques. As received powder is composed of mostly amorphous and a minor number of α-cristobalite phases. On annealing at higher temperatures amorphous phase gradually transforms to small crystallites of α-cristobalite. The tiny crystallites subsequently form small domains in the structural form of β-cristobalite. Silicosis is a chronic lung disease caused by breathing in tiny bits of silica dust. Silica is the second most common mineral in the earth's crust. It is a major component of sand, rock and mineral ores like quartz. People who work in jobs where they can be breathing in these tiny silica bits—like sandblasting, mining, construction and many others—are at risk for silicosis. When people breathe silica dust, they inhale tiny particles of silica that has crystallized. This silica dust can cause fluid build-up and scar tissue in the lungs that cuts down your ability to breathe. There are three types of silicosis: Chronic silicosis, the most common type of silicosis, usually occurs after 10 or more years of exposure to crystalline silica at low levels, Accelerated silicosis occurs 5-10 years after exposure and is caused by exposure to higher levels of crystalline silica. Acute silicosis can occur after only weeks or months of exposure to very high levels of crystalline silica. Acute silicosis progresses rapidly and can be fatal within months. Anyone with silicosis may suffer from several complications: Increased risk for lung infections and tuberculosis. Progressive massive fibrosis—severe scarring and stiffening of the lung, which makes it difficult to breathe. Progressive massive fibrosis can occur in either simple or accelerated silicosis, but is more common in the accelerated form with respiratory failure.

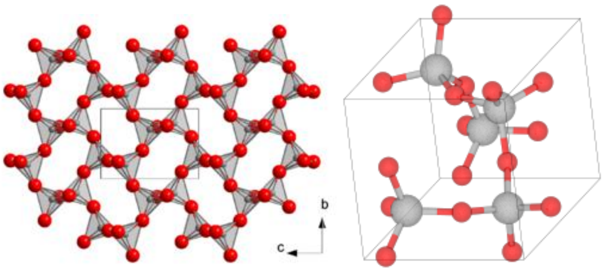
KEYWORDS: Nanocrystalline SiO_2, phase transformation, X-ray diffraction, electron diffraction, grain growth, silicosis, chronic simple silicosis, accelerated silicosis, complicated silicosis, acute silicosis, coniosis, scleroderma, SLE, PMF, leukotriene B4, cytokines.

INTRODUCTION

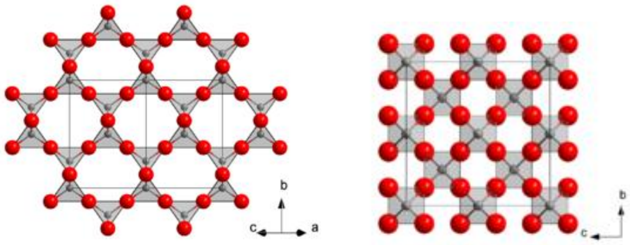
Silicon dioxide: Quartz, Silica, Silicic oxide, Silicon (IV) oxide, Crystalline silica, Pure Silica, Silicea, Silica sand Silicon dioxide [CAS No: 7631-86-9], Chemical formula: SiO_2, Molar mass: 60.08 g/mol, Appearance Transparent solid (Amorphous) White/Whitish Yellow (Powder/Sand), Density: 2.648 (α-quartz), 2.196 (amorphous) $g{\cdot}cm^{-3}$, Melting point: 1,713°C (3,115°F; 1,986 K) (amorphous), Boiling point: 2,950°C (5,340°F; 3,220 K), Magnetic susceptibility (χ): −29.6·10−6 cm^3/mol, Thermal conductivity: 12 (∥ c-axis), 6.8 (⊥ c-axis), 1.4 (am.) W/(m·K), Refractive index (nD): 1.544 (o), 1.553 (e)

Cristobalite is a mineral polymorph of silica that is formed at very high-temperatures. It is used in dentistry as a component of alginate impression materials as well as for making models of teeth. It has the same chemical formula as quartz, SiO2, but a distinct crystal structure. Both quartz and cristobalite are polymorphs with all the members of the quartz group, which also include coesite, tridymite and stishovite. Cristobalite occurs as white octahedra or spherulites in acidic volcanic rocks and in converted diatomaceous deposits in the Monterey Formation of the US state of California and similar areas. Cristobalite is stable only above 1470°C, but can crystallize and persist metastably at lower temperatures. It is named after Cerro San Cristóbal in Pachuca Municipality, Hidalgo, Mexico. The persistence of cristobalite outside its thermodynamic stability range occurs because the transition from cristobalite to quartz or tridymite is "reconstructive", requiring the breaking up and reforming of the silica framework. These frameworks are composed of SiO_4 tetrahedra in which every oxygen atom is shared with a neighbouring tetrahedron, so that the chemical formula of silica is

SiO_2. The breaking of these bonds required to convert cristobalite to tridymite and quartz requires considerable activation energy and may not happen on a human time frame. Framework silicates are also known as tectosilicates. There is more than one form of the cristobalite framework. At high temperatures, the structure is cubic, Fd3m, No. 227, Pearson symbol cF104. A tetragonal form of cristobalite (P41212, No. 92, Pearson symbol tP12) occurs on cooling below about 250°C at ambient pressure and is related to the cubic form by a static tilting of the silica tetrahedra in the framework. This transition is variously called the low-high or {\displaystyle \alpha {-}\beta }{\displaystyle \alpha {-}\beta } transition. It may be termed "displacive"; i.e., it is not generally possible to prevent the cubic β-form from becoming tetragonal by rapid cooling. Under rare circumstances the cubic form may be preserved if the crystal grain is pinned in a matrix that does not allow for the considerable spontaneous strain that is involved in the transition, which causes a change in shape of the crystal. This transition is highly discontinuous. The exact transition temperature depends on the crystallinity of the cristobalite sample, which itself depends on factors such as how long it has been annealed at a particular temperature. The cubic β phase consists of dynamically disordered silica tetrahedra. The tetrahedra remain fairly regular and are displaced from their ideal static orientations due to the action of a class of low-frequency phonons called rigid unit modes. It is the "freezing" of one of these rigid unit modes that is the soft mode for the α–β transition. In the α–β phase transition only one of the three degenerate cubic crystallographic axes retains a fourfold rotational axis in the tetragonal form. The choice of axis is arbitrary, so that various twins can form within the same grain. These different twin orientations coupled with the discontinuous nature of the transition can cause considerable mechanical damage to materials in which cristobalite is present and that pass repeatedly through the transition temperature, such as refractory bricks. When devitrifying silica, cristobalite is usually the first phase to form, even when well outside its thermodynamic stability range. This is an example of Ostwald's step rule. The dynamically disordered nature of the β-phase is partly responsible for the low enthalpy of fusion of silica.The micrometre-scale spheres that make up precious opal exhibit some x-ray diffraction patterns that are similar to that of cristobalite, but lack any long-range order so they are not considered true cristobalite. In addition, the presence of structural water in opal makes it doubtful that opal consists of cristobalite.



α-cristobalite



β-cristobalite

α-cristobalite is tetragonal whose Pearson symbol: tP12, P41212, No. 92. Density=2.334gm/cm^3. Crystalline form: Metastable form under normal pressure. β-cristobalite is cubic whose Pearson symbol: cF104, Fd3m, No.227. Crystalline form=Closely related to α-cristobalite; melts at 1978ºK, Category: Oxide mineral, quartz group. Formula: SiO_2, Strunz classification: 4.DA.15, Dana classification: 75.1.1.1, Crystal system: Tetragonal, Crystal class: Trapezohedral (422), Space group: P41212, P43212, Unit cell a = 4.9709(1) Å c = 6.9278(2) Å; Z = 4 (α polytype), Structure, Jmol (3D): Interactive image.

Identification: Color: Colorless, white, Crystal habit: Octahedra or spherulites up to several cm large, Twinning on {111}, Fracture: Conchoidal, Tenacity: Brittle, Mohs scale hardness: 6–7, Luster: Vitreous, Streak: White, Diaphaneity: Transparent, Specific gravity: 2.32–2.36, Optical properties: Uniaxial (−), Refractive index: nω = 1.487, nε = 1.484, Birefringence: 0.003, Pleochroism: None, Melting point: 1713°C (β)

Preamble: Mechanism of grain growth in nanocrystalline materials is an important area of studies for possible technological applications. Recently this problem has been addressed by various authors in different types of ceramic nanomaterials.[1-4] Although nanophase SiO_2 holds the possibility of wide range of applications.[5] Data base on the phase stability and growth of this material is not available. Phase transformations in crystalline SiO_2 have widely been studied and large volume of literatures both experimental as well as theoretical are available.[6-11] It is, therefore, of interest to undertake similar studies when this material is in nano-form. SiO_2 polymorph that is stable at ambient pressure and at temperatures between 1743ºK and its melting point near 1900ºK is the cubic β-cristobalite. The structure continues to exist in a metastable state at temperatures between 1743º and ~500ºK. Below 500ºK the structure adopts a tetragonal form, α-cristobalite which is also metastable. The temperature dependent behavior of both α and β crystobalites has been studied extensively and is reviewed by Hatch and Ghose[12] and Schmahl et. Al.[13] Till date various models on the mechanism of α to β transition have been developed.[14-16] However, the subject remains controversial because of the different structures of the high temperature polymorph (β-crystobalite).[14,17,18] Moreover, it has been shown that α-crystobalite structure and two structural variants of β-crystobalite are energetically almost degenerate over a rather wide range of densities.[10] Broadly speaking α to β transformation is interpreted as due to the relaxation of the atomic positions and cell parameters of the α-form with increase in temperature.[14] The transformation has also been interpreted as the α-form is shown to be a distorted form of the ideal cubic lattice of β-form.[10] The present work aims at studying temperature dependent structural transformation in nanophase SiO_2, and explores the possibility of using the existing models to explain the observed transformations.

Experimental: Nanopowder of SiO_2 synthesized by combustion flame chemical vapor condensation (CF-CVC)[19] has been used to study the temperature dependent behavior. Powder samples are annealed at 200, 400, 600, 800 and 1000°C for two hours in ambient conditions. X-ray measurements are done with a Philips (PW 1710) diffractometer. The diffraction data are recorded with CuK_{α} radiation while the tube is operated at 35 kV and current at 24 mA. For electron microscopic studies, samples are prepared first by making a colloidal suspension of the nanopowders in a solution of chloroform and formvar, and subsequently drying the solution on carbon coated copper grid. Copper grid with the dried sample is then inserted in a Philips (CM-12) transmission microscope for recording the diffraction and microscopic patterns. Samples heated at 200 and 400°C could not be used for the present studies as the samples after heat treatment were unstable. However, the samples heated at higher temperatures 600°C and above were found sable and have been used for the present studies. The Rietveld method[20] is used [LS_1 software used] to fit the experimental X-ray diffraction profiles with the theoretical diffraction patterns. Microstructural parameters like the crystallite size, lattice parameters, volume fraction of the component phases are obtained from the best fit of the generated X-ray diffraction pattern to the experimental pattern. Fourier coefficient of the strongest Bragg reflection is used to calculate the crystallite size. Errors in these parameters are the standard deviation computed by the built-in routine.[20] Estimated values of the standard deviations for the lattice parameters and the best-fit parameter (R values) are shown in Table-I.

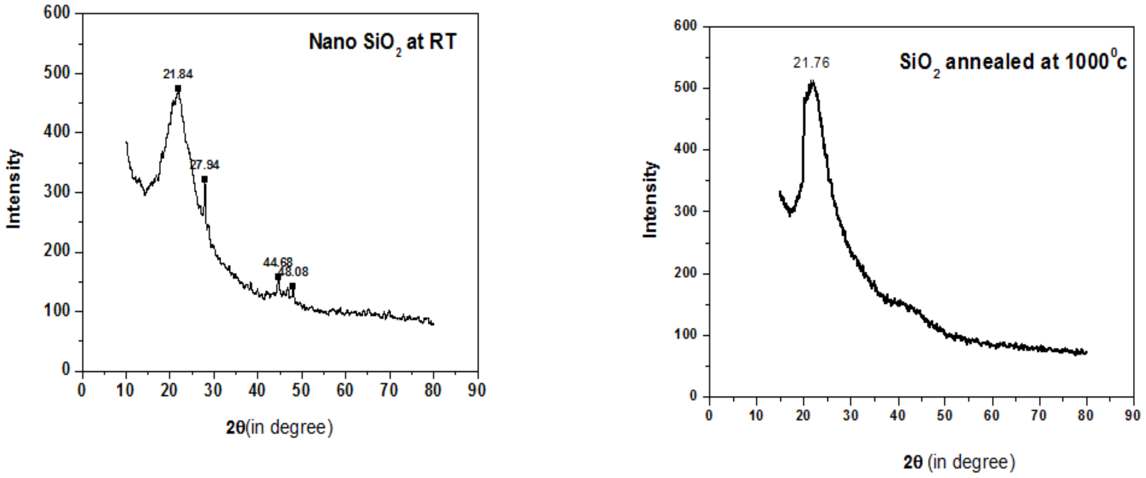


Figure-1 & 2.

RESULTS AND DISCUSSION

Figures 1 and 2 give the X-ray diffraction patterns of the nanopowder of SiO_2 at room temperature and the sample heated at 1000°C for 2 hours.

Table-I. Micro-structural parameters measured from XRD (SiO_2 Tetragonal).

T (0C)	D (nm)	a (nm)±std. deviation	c (nm) ± std. deviation	Good Ness of fit	Amorphous content %
25	3.0	$0.52882 \pm 1X10^{-5}$	$0.62943 \pm 3X10^{-5}$	1.26	94
600	2.5	$0.48773 \pm 2X10^{-5}$	$0.62900 \pm 2X10^{-5}$	1.33	91
800	4.0	$0.47973 \pm 1X10^{-5}$	$0.600 \pm 4X10^{-5}$	1.42	89
1000	4.0	$0.4725 \pm 5X10^{-5}$	$0.5896 \pm 3X10^{-5}$	1.40	86

Table-I gives the estimated values of the crystallite sizes, lattice parameters, concentration of amorphous phase. This table also gives the estimated values of the standard deviations in lattice parameters and the best fit parameter (R values) to indicate the closeness of the generated patterns (Rietveld technique using LS_1 software) to the experimental profiles. Figures-3 (a,b) give the transmission electron micrograph and diffraction pattern respectively for sample at room temperature. Figures-4 (a,b) give the corresponding patterns for samples heated at 600°C.

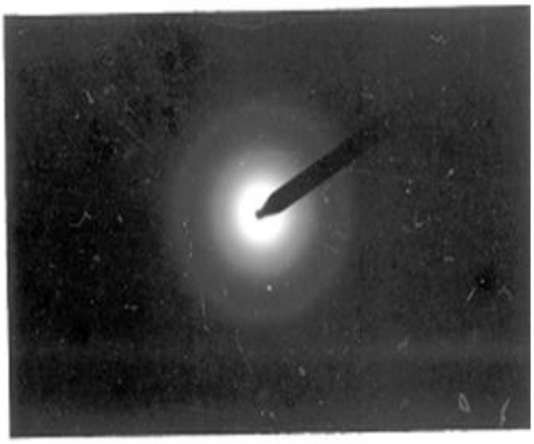


Figure-3a

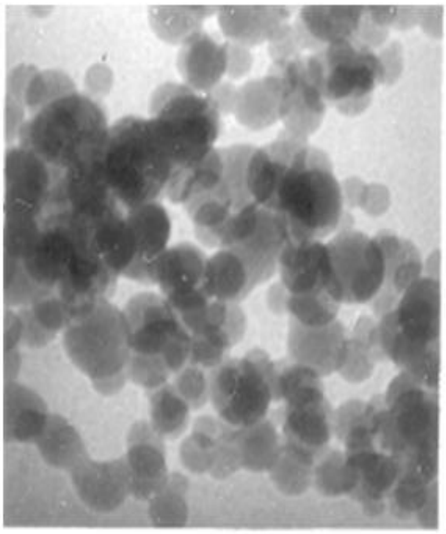


Figure-3b

Figure-3: (a) The transmission electron micrograph (120 kv, 100000 X) and (b) Electron diffraction pattern (120 kv) from one of the crystallites of as received samples.

Figure-4a

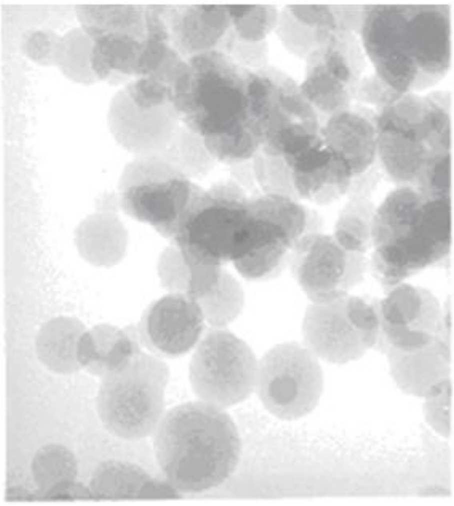


Figure-4b

Figure-4. (a) The transmission electron micrograph (120 kv, 100000 X) and (b) electron diffraction pattern (120kV) from one of the cristobalities of nano SiO2 sample annealed at 600^0 C.

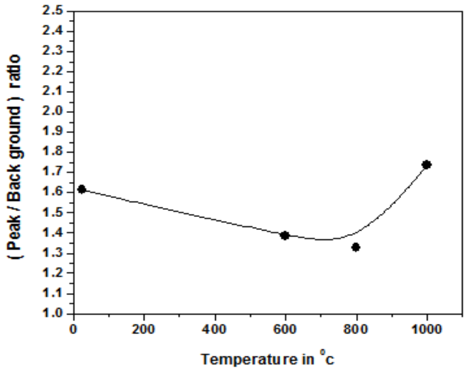


Figure-5

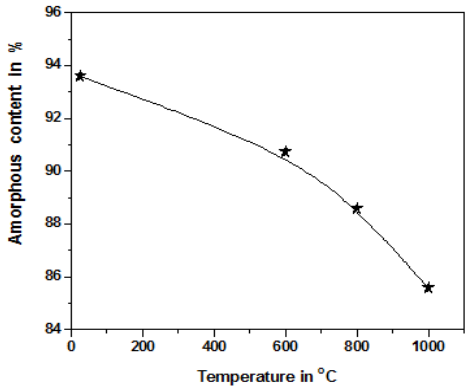


Figure-6

Figure-5 shows the change in the intensity ratio of the peak (Bragg angle 2θ ~ 22°) to the background with annealing.

Figure-6 gives the variation of the amorphous phase content with annealing. Figure-7 describes the relative change in the lattice parameters and volume change with temperatures.

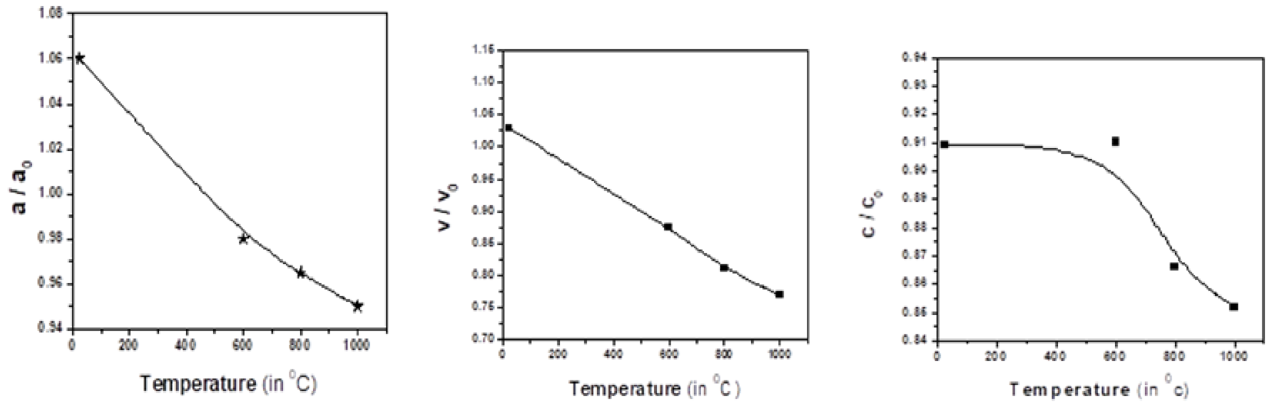


Figure-7a **Figure-7b** **Figure-7c**

Figure-7: The relative change in the lattice parameters with temperatures.

From the analysis of the X-ray powder diffraction pattern of the as received sample (Figure-1) it is observed that the sample consists of amorphous and crystalline phases. From Rietveld analysis (using the published values of the structural parameters of α-crystobalite (ICSD 32-1409) the crystalline phase is identified as the α-crystobalite. With annealing the amorphous phase content is found to decrease while the crystalline phase concentration increased. Crystallite sizes as measured from the Fourier analysis of the peak at 2θ ~ 22° (101) showed little change and are found to be extremely small. Decrease in amorphous phase content with annealing (Figure-6) and negligible increase in the sizes of the crystallites points out to the possibility of growth of a large number of small crystallites from amorphous phase. This is also evident from the increase in intensity of the (101) peak with annealing (Figure-5). Estimated values of the lattice parameters at room temperature (Table-1) correspond to the tetragonal phase of SiO_2. However, with annealing lattice parameters decreased (Figure-7). It is interesting to note that the nature of changes is similar to those reported for high pressure studies.[9] This could be due to the metastable nature of the α-crystobalite phase; it is also interesting to note that the tetragonal nature of the lattice is retained even at higher temperature of annealing. Again the electron diffraction pattern at room temperature (Figure-3b) is of amorphous type indicating that majority phase of the as received sample is amorphous which is also confirmed from X-ray estimates. The pattern recorded at 600°C (4b) is similar to that reported by Hua et al[7] except the presence of streaks. From the observed symmetry it has been concluded that the pattern corresponds to β-crystobalite recorded along (111) direction. However, Hua et al[7] observed existence of strong and characteristic diffuse scattering (appearance of streaks) above 275°C. This has been attributed due to dynamic rather than static origin and has been interpreted as the motions of the structure involving coupled rotations of the tetrahedral in columns along the (110) directions. Based on a Landau symmetry analysis on the α-β transition, Hatch and Ghose[12] proposed a similar the idea of the dynamical averaging. The observed weak diffuse scattering without streak (Figure-4b) has been attributed due to the formation of small domains of the tetragonal lattice resulting in the formation of the cubic lattice of β-crystobalite. This conclusion is based on the structural model proposed by Wright and Leadbetter[21] which has subsequently been supported by Liu et al[22] from ab initio total energy and lattice-dynamics calculations.

Silica: Silicon (Si) is the second most common element in the Earth's crust (oxygen is the most common). The compound silica, also known as silicon dioxide (SiO_2), is formed from silicon and oxygen atoms. Since oxygen and silicon make up about 75% of the Earth, the compound silica is quite common. It is found in many rocks, such as marble, sandstone, flint and slate and in some metallic ores. Silica can be a main component of sand. It can also be in soil, mortar, plaster and shingles. The cutting, breaking, crushing, drilling, grinding or abrasive blasting of these materials may produce fine silica dust. Silica occurs in 3 forms: crystalline, microcrystalline (or cryptocrystalline) and amorphous (non-crystalline). "Free" silica is composed of pure silicon dioxide, not combined with other elements, whereas silicates (e.g. talc, asbestos and mica) are SiO_2 combined with an appreciable portion of cations. Crystalline silica exists in 7 different forms (polymorphs), depending upon the temperature of formation. The main 3 polymorphs are quartz, cristobalite, and tridymite. Quartz is the second most common mineral in the world (next to feldspar). Microcrystalline silica consists of minute quartz crystals bonded together with amorphous silica. Examples include flint and chart. Amorphous silica consists of kieselgur (diatomite), from the skeletons of diatoms, and vitreous silica, produced by heating and then rapid cooling of crystalline silica. Amorphous silica is less toxic than crystalline, but not biologically inert, and diatomite, when heated, can convert to tridymite or cristobalite. Silica flour is nearly pure SiO_2 finely ground. Silica flour has been used as a polisher or buffer, as well as paint extender, abrasive, and filler for cosmetics. Silica flour has been associated with all types of silicosis, including acute silicosis. Silicosis is due to deposition of fine respirable dust (less than 10 micrometers in diameter) containing crystalline silicon dioxide in the form of alphaquartz, cristobalite, or tridymite.9 Diagnosis: There are three key elements to the diagnosis of silicosis. First, the patient history should reveal exposure to sufficient silica dust to cause this illness. Second, chest imaging (usually chest x-ray) that reveals findings consistent with silicosis. Third, there are no underlying illnesses that are more likely to be causing the abnormalities. Physical examination is usually unremarkable unless there is complicated disease. Also, the examination findings are not specific for silicosis. Pulmonary function testing may reveal airflow limitation, restrictive defects, reduced diffusion capacity, mixed defects, or may be normal (especially without complicated disease). Most cases of silicosis do not require tissue biopsy for diagnosis, but this may be necessary in some cases, primarily to exclude other conditions. For uncomplicated silicosis, chest x-ray will confirm the presence of small (< 10 mm) nodules in the lungs, especially in the upper lung zones. Using the ILO classification system, these are of profusion 1/0 or greater and shape/size "p", "q", or "r". Lung zone involvement and profusion increases with disease progression. In advanced cases of silicosis, large opacity (> 1 cm) occurs from coalescence of small opacities, particularly in the upper lung zones. With retraction of the lung tissue, there is compensatory emphysema. Enlargement of the hilum is common with chronic and accelerated silicosis. In about 5-10% of cases, the nodes will calcify circumferentially, producing so-called "eggshell" calcification. This finding is not pathognomonic (diagnostic) of silicosis. In some cases, the pulmonary nodules may also become calcified. A computed tomography or CT scan can also provide a mode detailed analysis of the lungs, and can reveal cavitation due to concomitant mycobacterial infection.

Figure-8: Silica & Silicosis.

Prevention: The best way to prevent silicosis is to identify work-place activities that produce respirable crystalline silica dust and then to eliminate or control the dust ("primary prevention"). Water spray is often used where dust emanates. Dust can also be controlled through dry air filtering. Following observations on industry workers in Lucknow (India), experiments on rats found that jaggery (a traditional sugar) had a preventive action against silicosis.

Treatment: Silicosis is an irreversible condition with no cure. Treatment options currently focus on alleviating the symptoms and preventing complications. These include: Stopping further exposure to silica and other lung irritants, including tobacco smoking, Cough suppressants, Antibiotics for bacterial lung infection. TB prophylaxis for those with positive tuberculin skin test or IGRA (Interferon-γ release assays) blood test. Prolonged anti-tuberculosis (multi-drug regimen) for those with active TB. Chest physiotherapy to help the bronchial drainage of mucus. Oxygen administration to treat hypoxemia, if present. Bronchodilators to facilitate breathing. Lung transplantation to replace the damaged lung tissue is the most effective treatment, but is associated with severe risks of its own. For acute silicosis, broncho-alveolar lavage may alleviate symptoms, but does not decrease overall mortality. Experimental treatments include: Inhalation of powdered aluminium, dpenicillamine and polyvinyl pyridine-N-oxide. Corticosteroid therapy. The herbal extract tetrandine may slow progression of silicosis.[23]

CONCLUSION

It has been experimentally demonstrated that nanophase SiO_2, synthesized from vapor phase, is initially composed of amorphous and a small fraction of crystalline α-crystobalite phases. On annealing at higher temperatures amorphous phase gradually transforms to small crystallites of α-crystobalite. The tiny crystallites subsequently form small domains in the structural form of β-crystobalite. Silicosis is a lung disease that is caused by inhaling tiny bits of silica. Silica is a common mineral that is part of sand, rock and mineral ores like quartz. People who work in jobs where they could breathe in these tiny silica bits—like sandblasting, mining, construction and many others—are at risk for silicosis. The silica dust can cause fluid build-up and scar tissue in the lungs that cuts down your ability to breathe. Silicosis cannot be cured, but you can prevent it if you take specific steps to protect yourself and your family.

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