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The Effect of Al_2O_3 , CaO , Cr_2O_3 and MgO on Devitrification of Silica

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THE EFFECT OF Al_2O_3 , CaO , Cr_2O_3 , and MgO
ON DEVITRIFICATION OF SILICA

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SUMMARY

The effect of doping on devitrification of vitreous silica was studied at 1100, 1200 and 1300 °C. Dispersion of dopants on a molecular scale was accomplished via sol-gel technique. All dopants accelerated the devitrification of silica but to different degrees. The most active was CaO followed by MgO , Al_2O_3 and Cr_2O_3 . Pure silica and silica containing Cr_2O_3 and Al_2O_3 devitrified to α -cristobalite only, whereas silica doped with CaO and MgO produced α -quartz and α -cristobalite. It appears that prolonged heat treatment would cause α -quartz to transform to α -cristobalite.

INTRODUCTION

Vitreous silica has been the subject of numerous investigations. Most of them were concerned with its structure (refs. 1 to 15). The original idea of the structure of vitreous silica was proposed by Zachariassen (ref. 1) from consideration of chemical composition. According to this random network (RN) theory, vitreous silica is built up of oxygen tetrahedra with the silicon atoms at their centers. The oxygen tetrahedra share corners in such a manner that an oxygen atom is linked to two silicon atoms. The relative orientation of tetrahedra may vary within rather wide limits. A much more precise description of the structure was obtained by using x-ray and neutron scattering techniques (refs. 2 to 5). The modern form of the RN theory (ref. 6) states that two molecular units are joined by a common, or bridging, oxygen atom (fig. 1). The Si-O-Si bond angle, θ , varies from bond to bond and may lie anywhere within a range of about 120° to 180°. Each molecular unit can lie in any position obtained by rotating it about its bridging Si-O bond so that the oxygens may assume many different sets of positions on the dotted circles, subject to restriction that the network remains continuously connected. The relative position of the circles themselves depends on the bond angle θ .

This concept underwent further modification (refs. 7 to 13) as a result of the discovery that vitreous silica is heterogeneous and contains ordered regions. Contrary to the findings of Narten (ref. 7) that packing of SiO_4 tetrahedra is similar to that of quartz, it has been reported (ref. 9) that the ordered regions are related to α -cristobalite. This has been confirmed recently (ref. 14) where it was shown that the tetrahedra of SiO_4 are arranged in polyhedra of six-fold rings, analogous to cristobalite. Additional evidence was provided by TEM observations of small crystalline regions (70 to 80 nm range) in vitreous silica, which were identified as α -cristobalite (ref. 15).

The work on the crystallization of vitreous silica at elevated temperatures (refs. 16 to 20) provides indirect evidence that the crystalline regions are indeed α -cristobalite, because pure vitreous silica was reported to devitrify to α -cristobalite. Attempts were also made to influence devitrification of vitreous silica by doping it with impurities (refs. 21 to 25). In these experiments, only the surface layer of silica was affected and devitrification proceeded from the surface inward. The growth of the cristobalite zone was found to be linear with time, implying that crystallization is a diffusionless process based on the reorientation of SiO_4 tetrahedra. Considering this structural picture of vitreous silica, it is of interest to determine the effect of dopants (impurities) on the crystallization process, especially when they are introduced on a molecular scale into a random network of SiO_4 tetrahedra. It is the purpose of this investigation to prepare doped vitreous silica by sol-gel technique and to study the effects of different dopants like Cr_2O_3 , Al_2O_3 , MgO and CaO , on the crystallization process. The reason for selecting Cr_2O_3 was that it does not form silicates and would be present in silica as Cr_2O_3 molecules whereas Al_2O_3 , MgO and CaO would form $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite), $\text{MgO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{SiO}_2$, which would be stable in silica matrix.

EXPERIMENTAL PROCEDURE

Preparation of Silica and Doped Silica Samples

The selected dopants were Cr_2O_3 , MgO , CaO , and Al_2O_3 . Their content is expressed in Table I as the ratio of silicon to doping element atoms (for example, in case of S-2 there is one chromium atom for 500 silicon atoms) and as weight percentage of an oxide in the silica. All the samples were synthesized by mixing tetraethoxysilane (TEOS), hydrated nitrates, ethyl alcohol, water, and hydrochloric acid in amounts indicated in Table II. Alcohol is used as the solvent for TEOS and water, which are mutually insoluble. The minute amounts of metal nitrates were dissolved in water, which then was acidified with HCl . These solutions were added to TEOS with admixed ethyl alcohol. Clear, homogenous solution resulted. The beaker containing the solution was covered and allowed to stand for gelling at room temperature. Gellation occurred within 24 hours. After that, the beaker was partially uncovered to permit evaporation of alcohol and water. The gels were allowed to dry under ambient conditions for several days which resulted in significant volume reduction and cracking. The drying procedure was continued at 120°C for 100 hr. These dried gels contained about 10 wt % water. To remove this water and decompose the nitrates, the dried gels, contained in platinum crucibles, were heated slowly in ambient atmosphere to 900°C for a period of not less than 24 hr. The product materials were now ready for crystallization experiments.

Crystallization Experiments

Crystallization experiments were performed at 1100 , 1200 , and 1300°C in ambient atmosphere. At 1100°C , the samples were heat treated for 5, 15, 30, and 50 hr; at 1200°C , for 3, 8, 16, 32 and 50 hr, and at 1300°C , for 3, 8 and 32 hr.

X-ray Diffraction Analysis

After each heat treatment, the samples were analyzed by the x-ray powder diffraction (XRD) method. The computer printout of a pattern for each sample listed 2θ angles, approximate width of the lines, intensity of the lines, intensity of the background, inter-planar spacing and normalized intensities. It should be noted that the intensity value for a diffraction line was the peak height rather than integrated intensity, which makes the data not completely quantitative. However, this gave sufficient accuracy for our observations. The relative amounts of α -cristobalite and α -quartz in a given sample were determined from a calibrated standard curve representing relative amounts of α -quartz and α -cristobalite as function of intensity ratio $I_{(101)\alpha\text{-crist.}}/I_{(101)\alpha\text{-quartz}}$ (fig. 2). This standard curve was prepared by determining intensity ratios of known cristobalite-quartz¹ powder mixtures.

RESULTS

The experimental data were obtained in the form of XRD charts and the corresponding computer printouts. Typical charts are shown in figures 3 to 5, which illustrate devitrification behavior of some samples. For example, in the case of pure silica (fig. 3) heat treated at 1200 °C for 3 hr, no devitrification occurred; after 50 hr, the (101) line of α -cristobalite could be observed. Figure 4 represents devitrification behavior of Sample S-4 in the same experimental conditions. After 3 hr, only a poorly developed α -cristobalite (101) line could be observed. After 50 hr, the same sample was completely devitrified. Figure 5 illustrates devitrification of Sample S-8 subjected to the same heat treatment. After 3 hr, vitreous silica containing CaO devitrified completely to α -cristobalite and α -quartz. One can observe from the intensity of the diffraction lines that after 50 hr the relative amount of α -quartz has decreased. Also the intensities of all diffraction lines of cristobalite and quartz were slightly reduced while the background intensity increased. The obtained XRD data were analyzed and summarized in the form of 12 tables, an example which is shown in Table III. The first column identifies the sample number and column 2 indicates the doping element and its concentration. For example, Cr-500 means that there are 500 silicon atoms per one chromium atom. Column 3 shows the ratio of intensity of the α -cristobalite (101) line ($I_{C(101)}$) and the background intensity (I_B). The number in the lower right corner of this column is the background intensity. Column 4 denotes the ratio of α -quartz (101) line intensity ($I_{Q(101)}$) with I_B , the corresponding background intensity. Column 5 indicates the calculated ratio of cristobalite and quartz content (C/Q) by weight. Any appropriate remarks concerning the degree of devitrification appear in the last column. A sample was considered fully devitrified when the background intensity near the α -cristobalite (101) line was similar to that of the rest of XRD pattern. For brevity, we do not show all 12 tables but their substance is discussed below.

Pure Silica (S-1)

Heat treatments at 1100° and 1200 °C for 50 hr were not sufficient to effect any degree of devitrification. Only after 8 hr at 1300 °C is a weak

¹High purity quartz powder was received courtesy of Quartz Scientific, Inc.

α -cristobalite (101) line observed. Even after 32 hr at 1300 °C, devitrification is not complete.

Silica + Chromia (S-2, S-3, S-4)

- 1100 °C No devitrification was observed in 50 hr. Only a weak α -cristobalite (101) was detected in S-3 and S-4.
- 1200° C The degree of devitrification was found to be an inverse function of chromia content. S-2 devitrified completely in 8 hr, while S-3 and S-4 devitrified in 16 hr. In each case, the product of devitrification was α -cristobalite only.
- 1300 °C S-2 devitrified completely in about 3 hr, whereas S-3 and S-4 were not fully crystalline after 8 hr. Continued heat treatments of S-2 and S-3 revealed unexpected behavior, namely, the diffraction line intensities (peak heights) of α -cristobalite decreased while in intensity of background increased. Only in the case of S-4 did the intensities of the diffraction lines increase while the intensity of the background decreased.

Silica + Magnesia (S-5, S-6)

Because magnesia reacts with silica to form silicates, it is expected that in samples a silica rich magnesium silicate, $MgO \cdot SiO_2$ would form. The observed effects are due to the presence of $MgO \cdot SiO_2$, the morphology of which, in the silica matrix, is not known.

- 1100 °C After 5 hr, there is evidence of devitrification to α -cristobalite and α -quartz. A higher degree of devitrification is noted in the sample (S-6) with higher MgO content. After 50 hr, S-5 is only partially devitrified, while S-6 is fully crystalline. At the beginning, α -quartz was the principal crystalline phase, however, after 50 hr, 90 percent of the crystalline phase was α -cristobalite and 10 percent was α -quartz.
- 1200 °C Here again, the sample with higher MgO content began to devitrify first forming α -quartz. Devitrification was complete within 32 hr. α -cristobalite represents 73 percent and α -quartz 27 percent of the total crystalline phases.
- 1300 °C The sample with a higher MgO content began to devitrify first. In contrast to heat treatment at 1100° and 1200°C, the crystalline phase to appear first was α -cristobalite. Complete devitrification was accomplished in 8 hr, after which time $I_{\alpha-c(101)}/I_B$ for S-5 has a greater value than for S-6. After 32 hr, the total crystalline phase composition was 90 percent α -cristobalite and 10 percent α -quartz.

Silica + Calcia (S-7, S-8)

According to the $CaO-SiO_2$ phase diagram, calcia should react with silica to form $CaO \cdot SiO_2$. The morphology of $CaO \cdot SiO_2$ in the silica matrix is not known.

- 1100 °C During the five hours, S-7 and S-8 devitrified partially to α -quartz and α -cristobalite. S-8 devitrified significantly faster than S-7. In both cases the predominant phase was quartz (90 percent). After 50 hr, only S-8 exhibited complete devitrification, α -quartz representing 67 percent of total crystalline phases, with α -cristobalite as the remainder.
- 1200 °C The higher content of CaO again promoted devitrification. Sample S-8 devitrified completely in 3 hr while Sample S-7 did so in 8 hr. For sample S-7, the relative amounts of α -cristobalite and α -quartz remained nearly constant throughout the entire heat treatment. S-8, after 50 hr, generated 55 percent α -quartz and 45 percent α -cristobalite. After 50 hr, the diffraction line intensity decreased while the background increased.
- 1300 °C At this temperature, devitrification of S-7 and S-8 was complete in 3 hr. Throughout the entire heat treatment at this temperature, α -cristobalite was the predominant phase. The approximate ratio of α -cristobalite to α -quartz was 10:1.

Silica + Alumina (S-9, S-10)

Doping silica with alumina results in the formation of mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ in the amorphous silica matrix. At the present time, the morphology of this mullite is not known.

- 1100 °C After 50 hr of heat treatment, both samples S-9 and S-10 devitrified slightly to α -cristobalite.
- 1200 °C Initially, both samples devitrified at the same rate regardless of alumina content. Only after 16 hr did S-10 devitrify faster than S-9. S-10 devitrified in 32 hr, while S-9 required 50 hr to do so.
- 1300 °C Nearly complete devitrification was obtained in three hr, regardless of Al_2O_3 content. Both samples devitrified completely, within 8 hr to α -cristobalite.

DISCUSSION

Considering the structure of vitreous silica (refs. 1 to 13) as a random network of interconnected SiO_4 tetrahedra exhibiting some degree of short range order, the introduction of dopants would be expected to have a significant effect on its properties. To accommodate a molecule of a dopant in the SiO_4 network, some bonds between tetrahedra must be broken and displacement of tetrahedra must occur. Consequently, the devitrification process, which in effect is a diffusionless reorientation of SiO_4 tetrahedra, might be made to occur more easily. One should expect that higher concentrations of dopants would cause more disruption in the SiO_4 network and thus enhance the devitrification rate. This was indeed found to be the case for MgO, CaO and Al_2O_3 or rather their silicates $\text{MgO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{SiO}_2$ and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. The exception to this model was presented by Cr_2O_3 . In general, the devitrification rate of silica doped with chromia was slower than that in the case of the other

dopants. However, the unusual thing about Cr_2O_3 as dopant, was the fact that silica with lower Cr_2O_3 content devitrified faster than silica with a higher Cr_2O_3 content. We have no explanation for this phenomenon. The only things that differentiate Cr_2O_3 from Al_2O_3 are the facts that Cr_2O_3 does not form silicates and Cr can have several valency states.

The observation that silica doped with CaO and MgO devitrified to α -quartz and α -cristobalite could be explained in the following manner. It is reasonable to assume that $\text{CaO}\cdot\text{SiO}_2$ and $\text{MgO}\cdot\text{SiO}_2$, dispersed in the matrix of amorphous silica, could act as catalysts for nucleation of α -quartz. However, because the concentration of dopants is sufficiently low, there could be regions of pure vitreous silica not affected by doping. This pure silica could devitrify slowly to α -cristobalite, whereas zones affected by dopants would devitrify to α -quartz, which not being stable at elevated temperature, should transform to α -cristobalite. The effect, during heat treatment the amount of α -cristobalite increased at the expense of α -quartz (fig. 4). This figure reveals also that prolonged heat treatment at elevated temperatures of already crystalline silica caused an increase in the background intensity of XRD pattern and a simultaneous intensity decrease of diffraction lines. It could be that this is caused by α -quartz \rightarrow α -cristobalite transformation. A disordered transition state could exist in α -quartz during this transformation causing an increase in the background intensity. The results obtained indicate that different dopants have different effects on the devitrification rate of silica. The most effective dopant was CaO followed by MgO, Al_2O_3 and Cr_2O_3 . Pure silica devitrified at the slowest rate. The question arises as to why CaO is more effective than MgO when their valencies and concentrations are the same. The silica rich silicates have the same formulas $\text{CaO}\cdot\text{SiO}_2$ and $\text{MgO}\cdot\text{SiO}_2$, respectively. The answer cannot be deduced from the present work. Kinetic and crystallographic studies at elevated temperatures could provide an answer to this question. None of the obtained XRD patterns revealed the presence of Cr_2O_3 , $\text{MgO}\cdot\text{SiO}_2$, $\text{CaO}\cdot\text{SiO}_2$ or $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. This could be due to the fact that the concentration of dopants was below the detectability threshold by XRD or the size of silicate particles was too small to diffract x-rays.

SUMMARY OF RESULTS

The effects of doping vitreous silica with Cr_2O_3 , CaO, MgO and Al_2O_3 was investigated to determine their role in devitrification. Sol-gel technique was used to prepare doped silica samples, the concentration of dopant being one atom per 125 atoms of silicon or less. All dopants promoted devitrification, CaO being the most active, followed by MgO, Al_2O_3 and Cr_2O_3 . Except for Cr_2O_3 , higher concentration of dopants increased devitrification rates. Silica doped with Cr_2O_3 and Al_2O_3 devitrified to α -cristobalite while CaO and MgO caused silica to devitrify to α -quartz and α -cristobalite.

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TABLE I. - COMPOSITION OF THE SAMPLES

Sample number	Ratio of silicon to doping element atoms	Dopant content in vitreous SiO ₂ , wt %
S-1	Pure silica	0
S-2	Si/Cr = 500	0.20 Cr ₂ O ₃
S-3	Si/Cr = 250	0.40 Cr ₂ O ₃
S-4	Si/Cr = 125	0.80 Cr ₂ O ₃
S-5	Si/Mg = 250	0.26 MgO
S-6	Si/Mg = 125	0.53 MgO
S-7	Si/Ca = 250	0.37 CaO
S-8	Si/Ca = 125	0.74 CaO
S-9	Si/Al = 250	0.34 Al ₂ O ₃
S-10	Si/Al = 125	0.67 Al ₂ O ₃

TABLE II. - Batch Compositions Used to Prepare Amorphous
And Doped Amorphous Silica Samples

Sample number	Si(OC ₂ H ₅) ₄ , g	Dopant and amount, g	C ₂ H ₅ OH, cc	Water, cc	HCl com, cc
S-1	52.082	0	28.0	18.0	1.0
S-2	↓	Cr(NO ₃) ₃ ·9H ₂ O 0.1600	↓	↓	↓
S-3	↓	Cr(NO ₃) ₃ ·9H ₂ O 0.3200	↓	↓	↓
S-4	↓	Cr(NO ₃) ₃ ·9H ₂ O 0.6400	↓	↓	↓
S-5	↓	Mg(NO ₃) ₂ ·6H ₂ O 0.2552	↓	↓	↓
S-6	↓	Mg(NO ₃) ₂ ·6H ₂ O 0.5104	↓	↓	↓
S-7	↓	Ca(NO ₃) ₂ ·4H ₂ O 0.2360	↓	↓	↓
S-8	↓	Ca(NO ₃) ₂ ·4H ₂ O 0.4720	↓	↓	↓
S-9	↓	Al(NO ₃) ₃ ·9H ₂ O 0.3752	↓	↓	↓
S-10	↓	Al(NO ₃) ₃ ·9H ₂ O 0.7504	↓	↓	↓

TABLE III. - SUMMARY OF RESULTS OBTAINED AFTER HEAT TREATMENT AT 1200 °C FOR 8 HR

Sample number	Si/DC	$\frac{I_{c(101)}}{I_B}$	$\frac{I_{Q(101)}}{I_B}$	C/Q, percent	Remarks
S-1	Pure SiO ₂	-----	-----	-----	Amorphous
S-2	Cr - 500	18.90/92	-----	-----	Complete devitrification to α-cristobalite
S-3	Cr - 250	10.40/104	-----	-----	Partial devitrification to α-cristobalite
S-4	Cr - 125	5.16/123	-----	-----	Even less complete devitrification to α-cristobalite
S-5	Mg - 250	3.49/161	0.82/137	90/10	Partially devitrified to α-cristobalite and α-quartz
S-6	Mg - 125	14.65/81	8.22/92	75/25	Complete devitrification to α-cristobalite and α-quartz
S-7	Ca - 250	6.00/110	10.94/102	56/44	Complete devitrification to α-cristobalite and α-quartz
S-8	Ca - 125	8.22/94	20.79/100	36/64	Complete devitrification to α-cristobalite and α-quartz
S-9	Al - 250	2.03/182	-----	-----	Amorphous, only a trace of α-cristobalite
S-10	Al - 125	2.09/172	-----	-----	Amorphous, only a trace of α-cristobalite

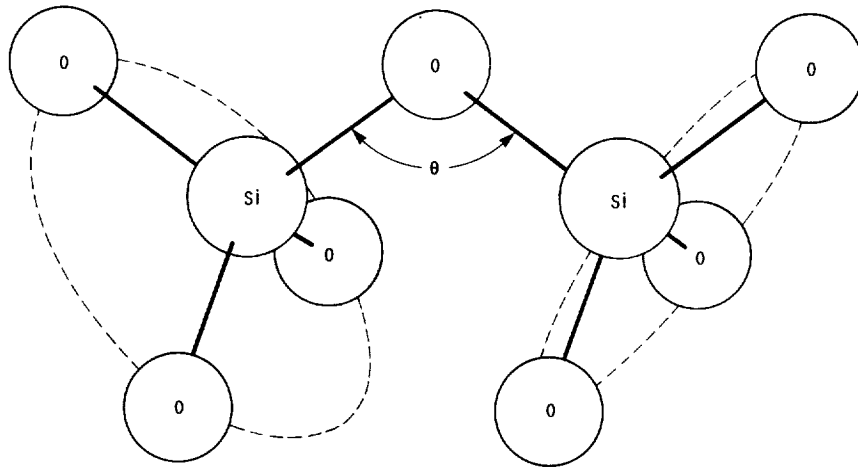


FIGURE 1. - SCHEMATIC REPRESENTATION OF TWO SiO_4 UNITS JOINED BY A COMMON OXYGEN ATOM (REF. 6).

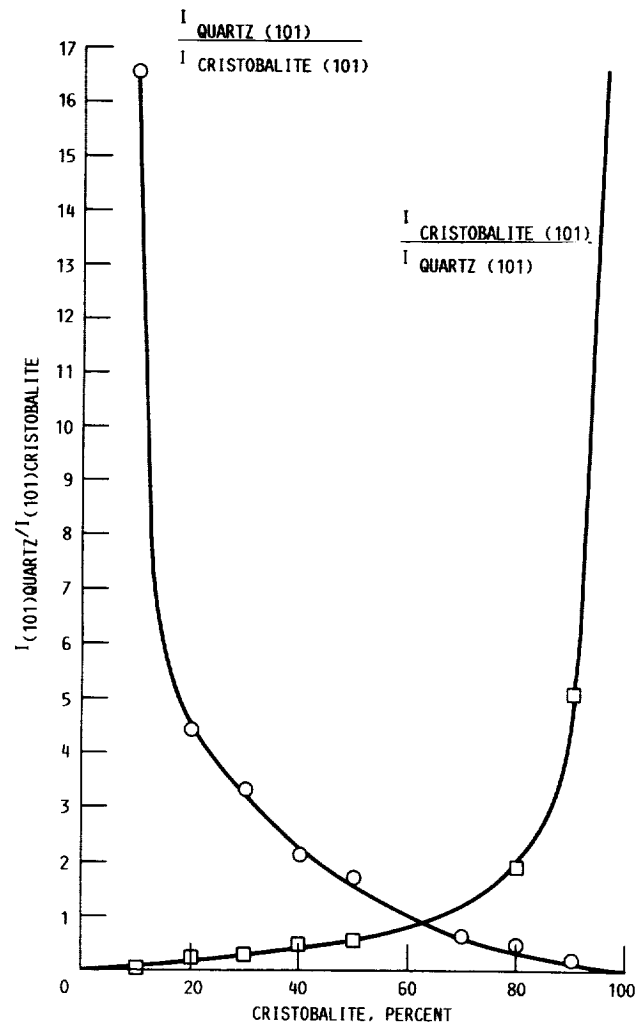


FIGURE 2. - MASTER PLOT FOR DETERMINATION OF RELATIVE AMOUNTS OF α -CRISTOBALITE AND α -QUARTZ.

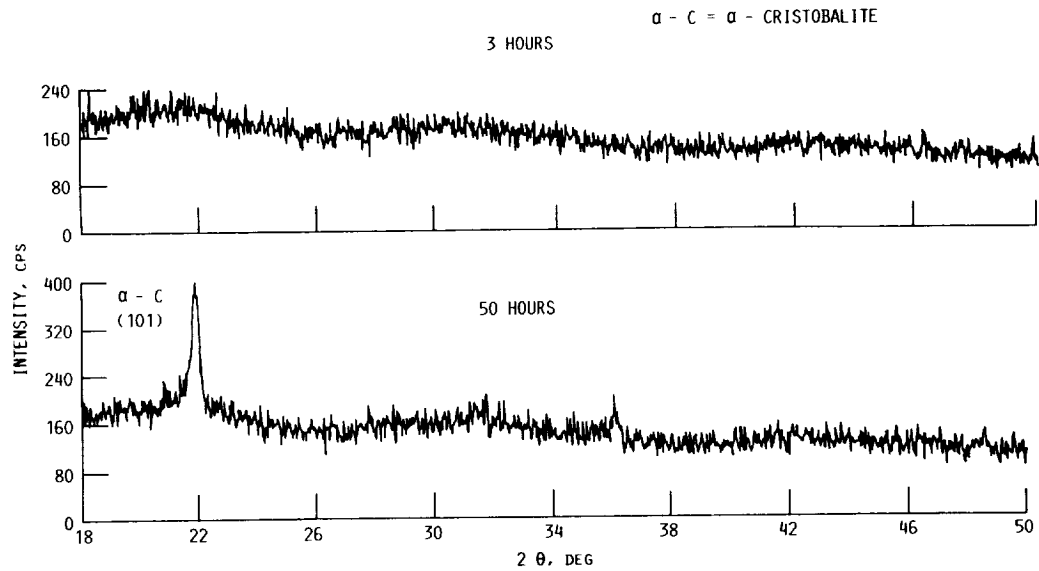


FIGURE 3. - XRD PATTERNS OF SAMPLE NO.1 HEAT TREATED AT 1200 °C FOR 3 AND 50 HOURS.

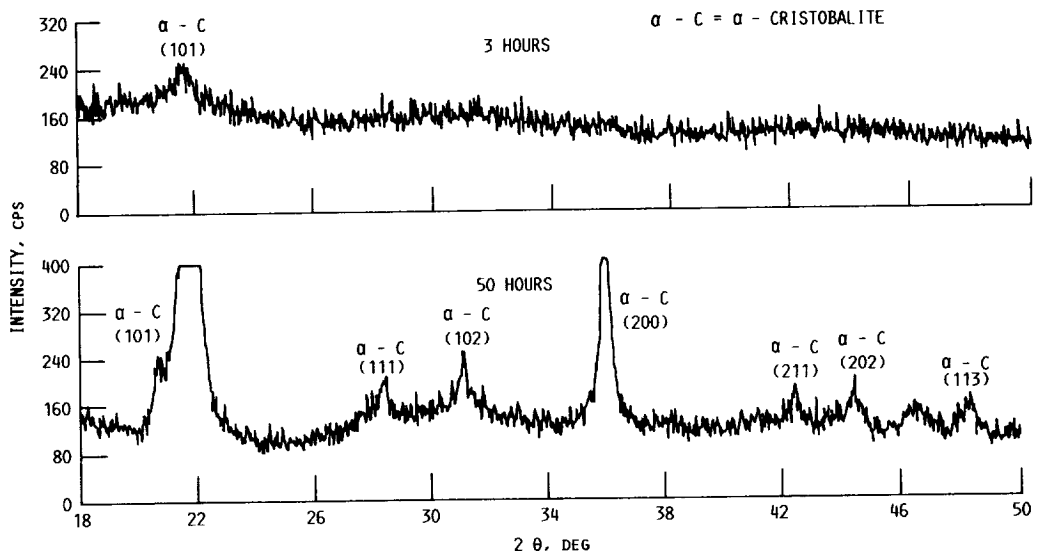


FIGURE 4. - XRD PATTERNS OF SAMPLE NO. 4 HEAT TREATED AT 1200 °C FOR 3 AND 50 HOURS.

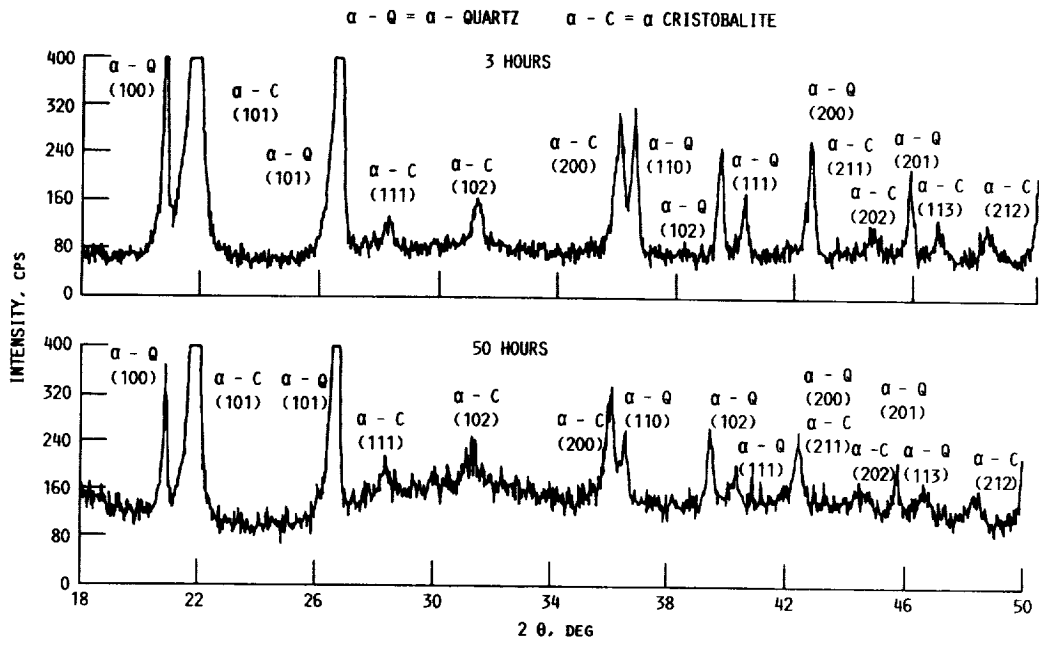


FIGURE 5. - XRD PATTERNS OF SAMPLE NO. 8 HEAT TREATED AT 1200 °C FOR 3 AND 50 HOURS.

1. Report No. NASA TM-101335		2. Government Accession No.		3. Recipient's Catalog No.	
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7. Author(s) Isidor Zaplatynsky				8. Performing Organization Report No. E-4350	
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12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546-0001				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract The effect of doping on devitrification of vitreous silica was studied at 1100, 1200 and 1300 °C. Dispersion of dopants on a molecular scale was accomplished via sol-gel technique. All dopants accelerated the devitrification of silica but to different degrees. The most active was CaO followed by MgO, Al ₂ O ₃ and Cr ₂ O ₃ . Pure silica and silica containing Cr ₂ O ₃ and Al ₂ O ₃ devitrified to α-cristobalite only, whereas silica doped with CaO and MgO produced α-quartz and α-cristobalite. It appears that prolonged heat treatment would cause α-quartz to transform to α-cristobalite.					
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