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# Spectroscopic Properties for High-pressure Polymorphs of Calcium and Strontium Metasilicates

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The IR spectra for the high-pressure polymorphs of alkaline-earth metasilicates, *viz.* $\alpha$-$CaSiO_3$, $\delta$-$CaSiO_3$, $\alpha$-$SrSiO_3$, $\delta$-$SrSiO_3$, and $\delta'$-$SrSiO_3$, which consist of cyclic anions, $(Si_3O_9)^{6-}$ or $(Si_4O_{12})^{8-}$ rings, were studied over a range of 1200—400 $cm^{-1}$. These silicates gave absorption bands in wavenumbers of about 1050—820 $cm^{-1}$, 750—620 $cm^{-1}$, and below about 580 $cm^{-1}$, based on symmetrical and anti-symmetrical stretches of Si–O bonds and Si–O bending modes for tetrahedral $SiO_4$ units, and Ca–O or Sr–O stretches. Among them, the bands characteristic of the silicate anions with ring structure in the $SrSiO_3$ polymorphs were found to shift to lower wavenumber with transformation into the $\delta'$ form. This suggests that the $(Si_4O_{12})^{8-}$ ring in $\delta'$-$SrSiO_3$ is less flexible than the $(Si_3O_9)^{6-}$ ring in the $\alpha$ or $\delta$ form. The experimental result that the quenching temperature of $\delta'$-$SrSiO_3$:$Eu^{2+}$ phosphor is higher than that of the $\delta$ form supports this consideration.

For most of silicates, the structure elements in crystal lattices are tetrahedral $SiO_4$ units, which are either isolated or connected with one another by sharing oxygens. The infrared absorption (IR) spectra of those silicates result from the stretching and bending modes for the Si–O bonds of $SiO_4$ units.[1)] Lazarev and coworkers[2)] have estimated the structures of silicate anions from the measurements of IR spectra.

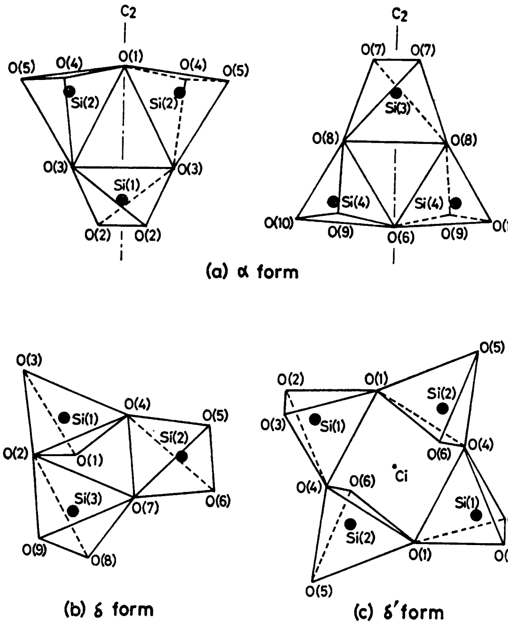
Alkaline-earth metasilicates show various polymorphisms under high-temperature and high-pressure.[3)] For example, $\alpha$- and $\beta$-$CaSiO_3$ (atmospheric high- and low-temperature forms) transform into $\delta$-$CaSiO_3$ above 30 kbar and 900 °C.[4)] The strontium metasilicate, $\alpha$-$SrSiO_3$, also give high-pressure phases, $\delta$- and $\delta'$-$SrSiO_3$, at 34—120 kbar and 750—1400 °C.[5)] Recently we have studied the luminescence properties for the high-pressure polymorphs of $CaSiO_3$:$Eu^{2+}$ and $SrSiO_3$:$Eu^{2+}$, and their emission intensities have been found to increase when the host lattice transforms into the high-pressure phases.[6)] Lattice vibrations of phosphors can be pointed out as one of quenching effects on luminescences.

In this paper, we study the IR spectra for the high-pressure polymorphs of $MSiO_3$ (M=Ca and Sr) and the temperature dependence for the luminescences of $SrSiO_3$:$Eu^{2+}$ polymorphs.

## Experimental

*Sample Preparation.* The preparation methods for the atmospheric and high-pressure phases of $MSiO_3$ and $MSiO_3$:$Eu^{2+}$ are described in Ref. 6.

*Optical Measurements.* The IR spectra of samples were obtained with a Hitachi Perkin-Elmer 225 grating spectrophotometer covering the range of 1200—400 $cm^{-1}$. Dry air was circulated through the spectrometer to eliminate the interference from atmospheric moisture. The samples dispersed in potassium bromide were examined using the pressed disk technique, and the mixtures containing 1.0 wt% samples were generally employed. Ultraviolet luminescence spectra were obtained with a Shimadzu recording absolute spectrofluorophotometer according to the techniques described elsewhere.[7)] The temperature dependence of luminescences was measured over the range between liquid $N_2$ temperature (77.4 K) and about 450 K in a stream of dry $N_2$ gas.



(a) α form

(b) δ form

(c) δ′ form

Fig. 1. Illustrations of silicate anions in the high-pressure polymorphs of $SrSiO_3$. These crystal structures have been reported in Refs. 5b and 6.

## Results and Discussion

*Silicate Anions.* In Table 1, we show the silicate anions in the high-pressure polymorphs of $CaSiO_3$ and $SrSiO_3$. Among these polymorphs, $\alpha$- and $\delta$-$CaSiO_3$ correspond to $\alpha$- and $\delta$-$SrSiO_3$, and hence the $\alpha$ or $\delta$ forms of $CaSiO_3$ and $SrSiO_3$ are approximately or entirely isostructural with each other. However, the $\delta'$ form is a characteristic phase of $SrSiO_3$ because $\delta'$-$CaSiO_3$ has not been obtained. The crystal lattices consist of $(Si_3O_9)^{6-}$ rings for the $\alpha$ or $\delta$ form and $(Si_4O_{12})^{8-}$ rings for the $\delta'$ form, respectively. The symmetries of these silicate anions are generally low.

In Fig. 1, we illustrate the silicate anions in $SrSiO_3$ polymorphs, of which the crystal structures have been reported in our previous papers.[5b,6)] The $(Si_3O_9)^{6-}$ rings of the $\alpha$ form show the symmetry of twofold rotation around an axis of Si(1)–O(1) or Si(3)–O(6) and the $(Si_4O_{12})^{8-}$ rings have inversion centers, but

TABLE 1. SILICATE ANIONS IN THE HIGH-PRESSURE POLYMORPHS OF $MSiO_3$ (M=Ca and Sr)

| Phase | Symmetry of crystal lattice[a)] | Silicate anion | Point group of anion | Ref. |
|---|---|---|---|---|
| α-$CaSiO_3$[b)] | Triclinic (P1 or P$\bar{1}$) | $(Si_3O_9)^{6-}$ ring | —<br>(pseudo $D_{3h}$) | 8 |
| δ-$CaSiO_3$ | Triclinic (P$\bar{1}$) | $(Si_3O_9)^{6-}$ ring | $C_1$ | 9 |
| α-$SrSiO_3$ | Monoclinic (C2) | $(Si_3O_9)^{6-}$ ring | $C_2$<br>(pseudo $D_{3h}$) | 5b |
| δ-$SrSiO_3$ | Triclinic (P$\bar{1}$) | $(Si_3O_9)^{6-}$ ring | $C_1$ | 6 |
| δ′-$SrSiO_3$ | Monoclinic ($P2_1/c$) | $(Si_4O_{12})^{8-}$ ring | Ci | 6 |

a) The space groups of polymorphs are given in parentheses. b) The detailed structure analysis of this phase has not been performed, but α-$CaSiO_3$ is approximately isostructural with α-$SrSiO_3$.

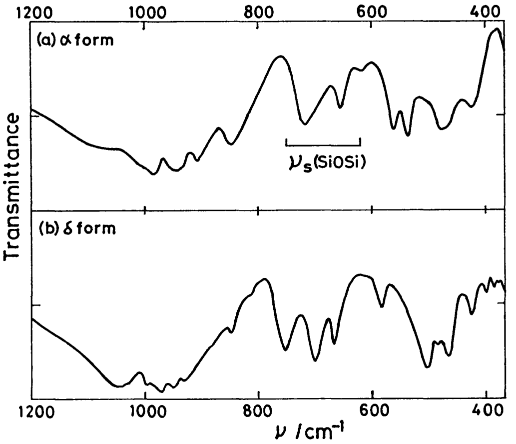


Fig. 2. IR spectra for the high-pressure polymorphs of $CaSiO_3$.

no symmetry element can be found out about the $(Si_3O_9)^{6-}$ rings of the δ form. Their point groups are $C_2$ (pseudo $D_{3h}$), $C_1$, and Ci for the α, δ, and δ′ forms, respectively. Consequently, the IR spectrum patterns of $CaSiO_3$ and $SrSiO_3$ polymorphs are expected to be very complex.

*IR Spectra.* For an isolated tetrahedral $SiO_4$ anions with a symmetry Td, there are four fundamental modes of vibrations, *viz.* a normally inactive symmetric stretch (800 cm$^{-1}$), an inactive doubly degenerate bend (500 cm$^{-1}$), a strongly active triply degenerate stretch (1050 cm$^{-1}$), and another active bending mode (625 cm$^{-1}$).[1)] When the $SiO_4$ units are connected with one another by sharing oxygens, the symmetric stretch of $SiO_4$ unit becomes an infrared active mode.

In Figs. 2 and 3, we show the IR spectra for the high-pressure polymorphs of $CaSiO_3$ and $SrSiO_3$, and in Table 2, their spectrum patterns are interpreted according to the assignments of some silicates attempted by Lazarev and co-workers.[2)] These metasilicates give strong absorptions over three regions around ≈580 cm$^{-1}$, 615—750 cm$^{-1}$, and 815—1070 cm$^{-1}$. The absorption bands of 815—1070 cm$^{-1}$ are derived from $\nu_{as}(O^-SiO^-)$, $\nu_{as}$(SiOSi), and $\nu_s(O^-SiO^-)$, where $\nu_{as}$ and $\nu_s$ correspond to the antisymmetric and symmetric stretching modes of $SiO_4$ unit, and $\nu(O^-SiO^-)$ and $\nu$(SiOSi) represent the Si–O bonds of oxygens non-shared and shared with the other $SiO_4$ units, respectively. The bands below 580 cm$^{-1}$ are responsible for the Si–O bending and Ca–O or Sr–O stretching modes. The group of bands in the regions of 615—750 cm$^{-1}$ corresponds to the mode originated from the $\nu_s$(SiOSi), which has been suggested to be a characteristic mode of the silicates containing cyclic anions by some workers.[10)] From the absorption bands around 615—750 cm$^{-1}$, consequently, we can obtain information for the ring structures of silicate anions in the high-pressure polymorphs of $CaSiO_3$ and $SrSiO_3$.

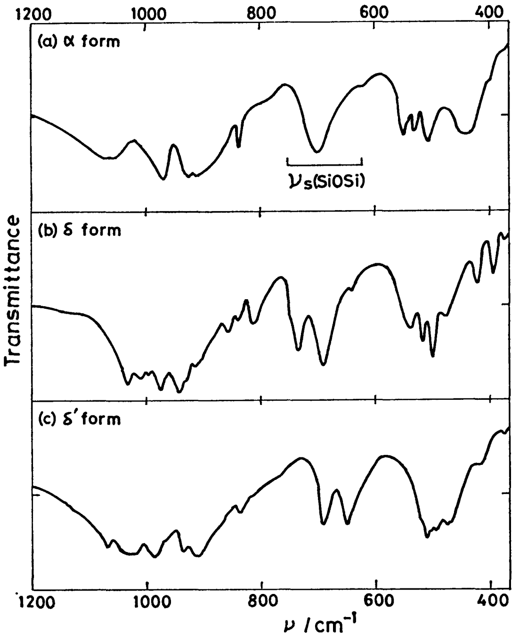


Fig. 3. IR spectra for the high-pressure polymorphs of $SrSiO_3$.

The IR spectrum patterns of δ-$CaSiO_3$ and δ-$SrSiO_3$, of which the crystal structures have been found to be entirely isostructural from the previous X-ray analyses,[6,9)] are closely similar to each other. For the α form, however, the spectrum profile around 615—750 cm$^{-1}$ for $CaSiO_3$ somewhat differs from that of $SrSiO_3$. The former silicate consists of three bands: 616, 653, and 717 cm$^{-1}$ whereas two bands: 622 and 705 cm$^{-1}$ are observed on the latter silicate. This suggests that the shapes of $(Si_3O_9)^{6-}$ rings in α-$CaSiO_3$ and α-$SrSiO_3$

TABLE 2. IR SPECTRA ($cm^{-1}$)[a] FOR THE HIGH-PRESSURE POLYMORPHS OF $MSiO_3$ (M=Ca and Sr)

| | $CaSiO_3$ | | $SrSiO_3$ | | |
|---|---|---|---|---|---|
| | $\alpha$ | $\delta$ | $\alpha$ | $\delta$ | $\delta'$ |
| | 1050 m | 1046 vs | 1067 s | 1033 vs | 1067 s |
| $\nu_{as}(O^{-}SiO)$ | 1003 s | 1031 s | 1053 s | 1007 s | 1025 vsb |
| | 985 vs | 1004 s | 970 vs | 997 s | 985 vs |
| $\nu_{as}(SiOSi)$ | 948 vs | 994 s | 925 vs | 976 vs | 968 s |
| | 940 vs | 972 vs | 910 vsb | 943 vs | 938 vs |
| $\nu_s(O^{-}SiO^{-})$ | 906 s | 949 vs | 840 m | 929 s | 910 vsb |
| | 846 s | 933 s | | 915 s | 840 w |
| | | 882 w | | 858 m | 816 vw |
| | | 847 w | | 842 w | |
| | | 817 w | | 816 m | |
| | 717 s | 753 s | 705 vsb | 749 m | 690 s |
| $\nu_s(SiOSi)$ | 653 m | 700 vs | 622 vw | 734 vs | 648 s |
| | 616 w | 666 s | | 692 vs | |
| | | | | 643 w | |
| Si–O bending and M–O stretching vibrations | 560 s | 581 m | 549 m | 535 m | 526 m |
| | 538 vs | 509 vs | 529 m | 519 s | 511 vs |
| | 474 sb | 484 m | 504 s | 502 vs | 505 s |
| | 421 w | 466 s | 436 sb | 485 s | 495 s |
| | | 425 m | | 480 s | 474 s |
| | | 400 w | | 476 s | 470 s |
| | | | | 421 m | 417 vw |
| | | | | 305 m | |

a) The characters of spectrum bands are represented as follows: v, very; s, strong; m, medium; w, weak; b, broad.

TABLE 3. LUMINESCENCE DATA FOR THE HIGH-PRESSURE POLYMORPHS OF $SrSiO_3$: $Eu^{2+}$ (1 atom%)

| Phase | $\lambda_{max}$/nm[a] | ($\lambda$/2)/nm[b] | Q.E./%[c] | $T_{50}$/K[d] |
|---|---|---|---|---|
| $\alpha$ | 498 | 75—80 | <1 | 380 |
| $\delta$ | 503 | 63 | 6 | 300 |
| $\delta'$ | 466 | 58 | 37 | 360 |

a) $\lambda_{max}$=peak position of the emission band at 300 K. b) $\lambda/2$=half-width of emission band. c) Q.E.=quantum efficiency under an optimum excitation at 300 K. d) $T_{50}$=quenching temperature at which the intensity of the luminescence is half of that at 77 K.

are similar but their symmetries are distinct from each other. The symmetries of crystal structures are generally higher than those of structure elements, *e.g.* silicate anions, in crystal lattices. From Table 1, the symmetry for the $(Si_3O_9)^{6-}$ ring in $\alpha$-$CaSiO_3$ is expected to be low compared with that for $\alpha$-$SrSiO_3$, and possibly the silicate anion in $\alpha$-$CaSiO_3$ does not show the symmetry of two-fold rotation. This must be confirmed if the detailed structure analysis of $\alpha$-$CaSiO_3$ is performed.

For the $\delta'$ form, the IR spectrum profile responsible for the mode of $\nu_s$(SiOSi) consists of two strong bands at about 648 and 690 $cm^{-1}$, which shift to longer wavenumber compared with the main absorption bands of $\alpha$- or $\delta$-$SrSiO_3$. This observation suggests that the ring of $(Si_4O_{12})^{8-}$ anion is less flexible than that of the $(Si_3O_9)^{6-}$ anion in $\alpha$- or $\delta$-$SrSiO_3$.

*Luminescence Properties of $SrSiO_3$:$Eu^{2+}$.* In Table 3, we summarize the luminescence properties of $SrSiO_3$: $Eu^{2+}$ modifications. The polymorphs of $SrSiO_3$:$Eu^{2+}$ give various emissions colored with blue or green,[6] and the emission intensity considerably increases when the host lattice has transformed into high-pressure phases. As one of quenching effects on luminescences, we can point out the lattice vibration of phosphors, and the luminescences are generally quenched when the temperature of phosphors is raised. The temperature dependences for the emission intensities of $SrSiO_3$: $Eu^{2+}$ polymorphs are shown in Fig. 4. The shape of quenching curve observed on $\alpha$-$SrSiO_3$:$Eu^{2+}$ differs from those for the $\delta$ and $\delta'$ forms. Since the emission of the $\alpha$ form is very weak and the quenching curve is unreliable, however, we are possibly unable to obtain any information from this observation. The $\delta$

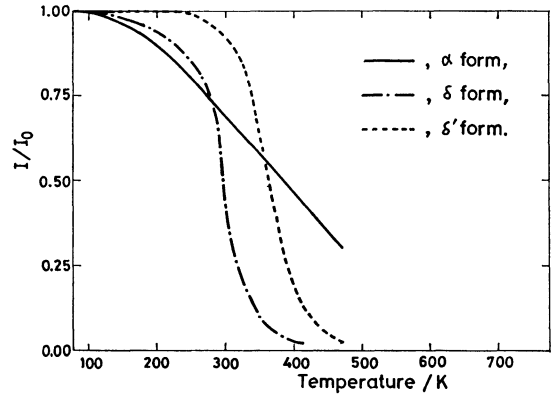


Fig. 4. Temperature dependences of the light output of $SrSiO_3$: $Eu^{2+}$ (1 atom%) polymorphs.

and $\delta'$ forms give the shapes of quenching curves similar to each other, of which the results are reasonable and well reliable.

It is noticeable that the $T_{50}$ value of $\delta'$-$SrSiO_3$:$Eu^{2+}$ (*ca.* 360 K) is higher than that of $\delta$-$SrSiO_3$:$Eu^{2+}$ (*ca.* 300 K). This means that, in $\delta'$-$SrSiO_3$:$Eu^{2+}$, the quenching effect caused by the lattice vibration is to be smaller than that in the $\delta$ form. Since the silicate anions can be regarded as mainly taking part in the lattice vibration of the crystals, the $(Si_4O_{12})^{8-}$ ring in the $\delta'$ form must be hard to vibrate compared with the $(Si_3O_9)^{6-}$ ring in the $\delta$ form. This agrees with the information obtained form the IR spectrum measurements. Therefore, $\delta'$-$SrSiO_3$:$Eu^{2+}$, which consists of the rigid $(Si_4O_{12})^{8-}$ rings give the relatively strong emission. The experimental result that the emission intensity of $\alpha$-$SrSiO_3$:$Eu^{2+}$ has been very weak is interpreted on the basis of a quenching effect *via* energy transfers between the neighboring $Eu^{2+}$ ions.6)

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