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Electron and X-Ray Diffraction, and ^{29}Si MAS NMR Studies of the Solid Solution $Cs_4Sb_4O_8(Si_{4(1-x)}Ge_{4x}O_{12})$

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The solid solution $Cs_4Sb_4O_8(Si_{4(1-x)}Ge_{4x}O_{12})$ has been studied using electron and X-ray diffraction, and ^{29}Si MAS NMR. All compositions for $0 \le x \le 1$ were found to be single phase. However, the *mmm* symmetry of the X_4O_{12} rings is maintained for $x \le 0.15$. Structure determinations from single crystals corresponding to $x = 0.5$ and 0.6 indicate a random distribution of Si (and Ge) atoms on the tetrahedral X sites. Analysis of the ^{29}Si MAS NMR spectra shows that the statistical distribution of Si (and Ge) atoms in the X_4O_{12} rings is equally present at a local level.

INTRODUCTION

Previous investigations on a series of isomorphous antimony cyclotetrasilicates and cyclotetragermanates $A_4Sb_4O_8(X_4O_{12})$ (A = K, Rb, Cs, Tl; X = Si, Ge) have shown that the three-dimensional $[Sb_4O_8(X_4O_{12})]^{4-}$ framework is rather flexible (1). This is illustrated in Fig. 1 which shows a fragment of this framework in the Cs, Rb, and K antimony cyclotetrasilicate structures. The most symmetrical arrangement is observed for the Cs phase with a true *mmm* symmetry for the cyclotetrasilicate group. For the smaller alkali ions, a progressive distortion of the framework is observed along with a lowering of the symmetry. Such distortions tend to adjust the size of the channels to that of the alkali ions. They are of course limited by the constraint that the SbO_6 and SiO_4 polyhedra remain rather regular. Consequently for the Na analogue that is prepared via an ion exchange reaction, there is no further distortion, but the compound is hydrated (2). In a similar way, the $[Sb_4O_8(Ge_4O_{12})]^{4-}$ framework corresponding to the Cs phase exhibits a distortion with respect to the $[Sb_4O_8(Si_4O_{12})]^{4-}$ framework in $Cs_4Sb_4O_8(Si_4O_{12})$; this distortion tends to minimize the volume increase that one would expect from the replacement of SiO_4 tetrahedra by GeO_4 tetrahedra, thus allowing Cs to lie in sites of more adequate size (1). Thus, if one refers to the symmetry of its framework, the crystal structure of $Cs_4Sb_4O_8(Si_4O_{12})$ seems to be an exception when compared with that of other members of the series. At this point, one wonders whether the *mmm* symmetry of the X_4O_{12} ring only exists for a unique composition within this structural family or if it can be maintained in a solid solution domain. In order to answer this question, a study of the solid solution $Cs_4Sb_4O_8(Si_{4(1-x)}Ge_{4x}O_{12})$ has been undertaken with the aim, among others, of analyzing the distribution of SiO_4 and GeO_4 tetrahedra in the X_4O_{12} rings through the use of electron and X-ray diffraction, and ^{29}Si MAS NMR.

EXPERIMENTAL

Synthesis

Polycrystalline samples were prepared by solid state reaction from stoichiometric mixtures of $CsNO_3$, $Sb_2O_5 \cdot xH_2O$, SiO_2, and GeO_2 heated in air for 12 hr at 1473 K. Attempts to grow single crystals were undertaken from mixtures of the same reactants but with a twofold excess of $CsNO_3$ and $Sb_2O_5 \cdot xH_2O$. The mixtures were heated for 1 hr at 773 K and then at 1623 K for 3 hr. Single crystals were obtained for two compositions ($x = 0.5$ and 0.6) which were verified by a chemical analysis conducted with an electron microprobe; they are thin colorless square plates.

Diffraction and NMR Studies

It has already been shown (1), that $Cs_4Sb_4O_8(Si_4O_{12})$ crystallizes in the tetragonal system, space group $P4_2/mmc$, whereas $Cs_4Sb_4O_8(Ge_4O_{12})$ exhibits, due to the distortion mentioned above, a superstructure leading to an I-centered unit-cell (space group $I4_122$) with a' and c' parameters related to the a and c parameters of $Cs_4Sb_4O_8(Si_4O_{12})$ as follows:

$$a' \sim a\sqrt{2} \text{ and } c' \sim 2c.$$

In order to determine whether the (Si, Ge) solid solu-

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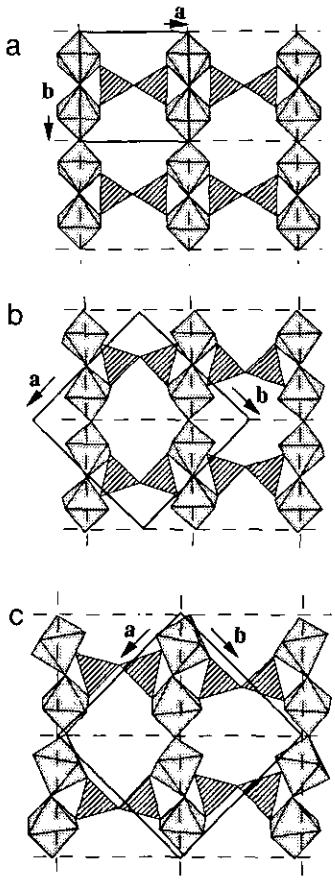


FIG. 1. [001] view of a fragment of the $[Sb_4O_8(X_4O_{12})]^{4-}$ framework in (a) $Cs_4Sb_4O_8(Si_4O_{12})$, (b) $Rb_4Sb_4O_8(Si_4O_{12})$ (or $Cs_4Sb_4O_8(Ge_4O_{12})$), and (c) $K_4Sb_4O_8(Si_4O_{12})$.

tions exhibit superstructures or not, electron diffraction experiments were performed with the use of a JEOL 100CX electron microscope. No superstructure reflections were observed with $x \leq 0.15$, thus indicating that the symmetry of X_4O_{12} rings could remain *mmm* with 15% of SiO_4 tetrahedra substituted by GeO_4 tetrahedra. Accordingly, single-crystal X-ray studies of compositions with $x = 0.5$ and 0.6 uniquely determine their space group as $I4_122$.

On the basis of X-ray powder patterns, all compositions for $0 \leq x \leq 1$ were found to be single phases. The cell parameters were refined by a least-squares procedure from powder diffraction data collected with an Inel curved multidetector (0.2-mm capillary, $\lambda(CuK\alpha_1) = 1.54059$ Å, silicon as standard). Figure 2 shows their variation as a function of composition x (in this representation, a and c for $x = 0$ have been multiplied by $\sqrt{2}$ and 2, respectively).

Intensity data for two single crystals corresponding to $x = 0.5$ and 0.6, respectively, were collected with a Nonius CAD4 diffractometer operating under the conditions

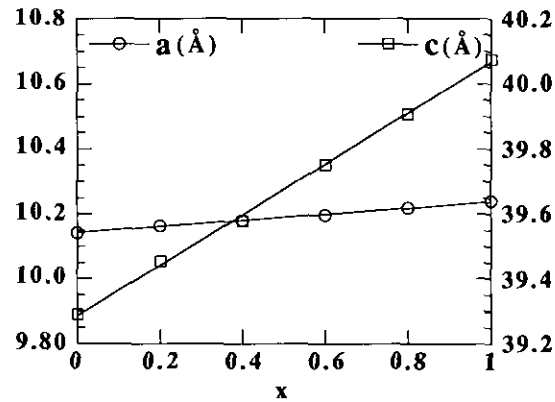


FIG. 2. Variation of the lattice parameters as a function of x.

given in Table 1. For the data reduction, absorption corrections (Gaussian), structure solution and refinement, the MoLEN program chain of Enraf-Nonius (3) was used.

The NMR acquisition conditions are reported in Table 2.

STRUCTURE DETERMINATIONS

For both compositions ($x = 0.5$ and 0.6) the initial positions of atoms were taken from the structure of $Cs_4Sb_4O_8(Ge_4O_{12})$ (1) and the occupancy of the tetrahedral X sites by Si and Ge atoms was refined.

For $x = 0.6$, anisotropic temperature factors were assigned to Cs and Sb atoms. After refinement, the B values for some oxygen atoms are low. This is due to the strong correlations that exist between B factors for atomic positions labeled with the same numbers. As a matter of fact, such positions are inferred from a given position in the more symmetrical structure of $Cs_4Sb_4O_8(Si_4O_{12})$ (1).

For $x = 0.5$, owing to the lower Ge content and the smaller size of the crystal, the superstructure reflections were weaker and those that were correctly measured

TABLE 1
Data Collection and Final Refinement Conditions

	$x = 0.6$	$x = 0.5$
Crystal size (mm)	*0.02 × 0.12 × 0.12*	*0.006 × 0.08 × 0.08*
Radiation (Å)	Mo$K\alpha$, $\lambda = 0.71069$	Mo$K\alpha$, $\lambda = 0.71069$
Scan mode	ω	ω
Scan angle (°)	$\Delta\omega = 1.0 + 0.35 \tan\Theta$	$\Delta\omega = 1.0 + 0.35 \tan\Theta$
Recording angular range (Θ°)	1.5–30	1.5–35
Number of independent reflections with $\sigma(I)/I < 0.33$ (used in refinements)	1115	878
Number of variables	92	80
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.037	0.042
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_o^2]^{1/2}$ with	0.038	0.042
$w = 1/(1 + [(F_{obs} - F_{ave})/F_{max}]^2)$		
Extinction parameter g	$2.46(8) \times 10^{-8}$	$1.21(9) 10^{-8}$

TABLE 2
NMR Acquisition Conditions

Field	7 T
Spectrometer	Bruker MSL 300
Probehead	Bruker MAS 7 mm
Nucleus	^{29}Si
Nucleus spin number	1/2
Resonance frequency	59 MHz
Pulse length	5 msec
Pulse angle	90°
Dead time	5 msec
Recycle time	4 sec
Spectral width	15 kHz
MAS spinning speed	4 kHz
Number of scans	10^3 to 10^5
Digitized points	8192
Reference as 0 ppm	Tetramethylsilane
Solid test sample	Polydimethylsilane

($I > 3\sigma(I)$) were less numerous; thus anisotropic temperature factors were assigned only to the Cs atoms. After refinement, it appears that B is low (0.18(4) Å^2) for the Ge, Si(1) site and high (0.70(4) Å^2) for Ge, Si(1'), suggesting a possible problem with the occupancy refinements. A refinement with fixed B values of 0.4 Å^2 for both sites was then undertaken. It led to occupancies of 0.51(1) for Ge(1) and 0.49(1) for Ge(1'), i.e., values not significantly different from those obtained without constraint on B factors.

As already observed in $Cs_4Sb_4O_8(Ge_4O_{12})$ (1), B factors for Cs(1) in both structures are higher than those of other Cs positions. This is probably due to some delocalization of the cation within this site. As a matter of fact, for the Cs(1) position in $Cs_4Sb_4O_8(Si_4O_{12})$, the electron density is better accounted for when an 8q position, close to the origin, is statistically occupied (1).

Table 1 shows the main results of the final refinements that include corrections for secondary extinction and account for anomalous dispersion.

The final Fourier difference maps are featureless with maxima and minima in the range of ± 1.2 eÅ^{-3}. Tables 3 and 4 present the final atomic coordinates, thermal parameters, and occupancy of the X sites (structure factor tables are available from the authors upon request).

After refinement, the occupancies of the X sites in both phases are in good agreement with the compositions inferred from the chemical analysis. Furthermore, they indicate a random distribution of Si and Ge atoms on these sites.

The bond distances and bond angles around Cs and Sb atoms are very close to those already calculated in the structures of the end members of the solid solution, while the X–O distances are intermediate between typical Si–O and Ge–O distances. The average $<X$–O$>$ distances within the XO_4 tetrahedra are given for $x = 0.5$ and 0.6 in Table 5 along with those for the end members (tables of bond distances and bond angles are available from the authors upon request).

Although the results of the two previous structural determinations lead to a random distribution of Ge (and Si) atoms on the two tetrahedral sites of the structure, they do not indicate anything about the local environments which can, however, be determined by NMR measurements; in other words, an average statistical distribution inferred from an X-ray analysis can result in several types of local nonstatistical distributions that NMR can theoretically distinguish.

ANALYSIS OF ^{29}Si MAS NMR SPECTRA

Since NMR is sensitive to the local environment of the nucleus under study, the appearance of the spectra is determined mainly by the distribution of oxygen atoms around Si. However, because each oxygen atom around a given Si is linked to two cations, the local environment is actually governed by the four nearest neighbor cations.

TABLE 3
$Cs_4Sb_4O_8[(Si_2Ge_2)O_{12}]$: Fractional Atomic Coordinates and Thermal Parameters

Atom	Occupancy	x	y	z	B^*_{iso}, B_{eq}(Å^2)
Cs(1)	1	0.2652(2)	0.7348	0	2.46(3)
Cs(2)	1	0	0	0.42973(5)	1.18(4)
Cs(2')	1	0	0	0.06702(5)	1.18(4)
Cs(3)	1	0.2534(4)	0.25	0.125	1.15(3)
Sb(1)		0.3803(2)	0.8670(2)	0.09084(3)	0.39(2)*
Sb(1')	1	0.3671(2)	0.8797(2)	0.59429(3)	0.33(2)*
Ge(1)	0.48(1)	0.3596(4)	0.1307(4)	0.03935(7)	0.18(4)*
Si(1)	0.52				
Ge(1')	0.53(1)	0.3682(3)	0.1401(3)	0.54213(8)	0.70(4)*
Si(1')	0.47				
O(1)	1	0.248(2)	0.947(2)	0.1200(4)	0.6(1)*
O(1')	1	0.25	0.950(3)	0.375	0.6(1)*
O(1'')	1	0.25	0.946(3)	0.875	0.6(1)*
O(2)	1	0.203(2)	0.476(2)	0.0645(4)	0.7(3)*
O(2')	1	0.518(2)	0.793(2)	0.0593(4)	0.5(3)*
O(2'')	1	0.321(1)	0.978(1)	0.0523(5)	0.7(2)*
O(2''')	1	0.020(2)	0.679(2)	0.0566(5)	0.7(2)*
O(3)	1	0.403(2)	0.132(2)	0.9991(5)	1.6(3)*
O(4)	1	0.221(2)	0.219(2)	0.0460(4)	1.4(3)*
O(5)	1	0	0.5	0.1099(5)	0.7(3)*
O(5')	1	0.5	0	0.1070(6)	1.0(4)*
O(6)	1	0.261(2)	0.730(2)	0.0733(3)	0.6(2)*

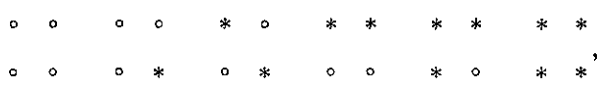
Note. Starred atoms (*) were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent parameter.

TABLE 4
$Cs_4Sb_4O_8[(Si_{8/5}Ge_{12/5})O_{12}]$: Fractional Atomic Coordinates and Thermal Parameters

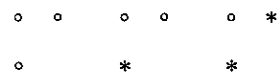
Atom	Occupancy	x	y	z	B^*_{iso}, B_{eq}(Å^2)
Cs(1)	1	0.2655(2)	0.7345	0	2.57(2)
Cs(2)	1	0	0	0.42935(4)	1.11(3)
Cs(2′)	1	0	0	0.06685(4)	1.37(3)
Cs(3)	1	0.2534(3)	0.25	0.125	1.17(2)
Sb(1)	1	0.3792(1)	0.8682(1)	0.09094(2)	0.46(2)
Sb(1′)	1	0.3649(1)	0.8814(1)	0.59438(2)	0.32(2)
Ge(1)	0.606(8)	0.3591(3)	0.1293(3)	0.03941(5)	0.40(3)
Si(1)	0.394				
Ge(1′)	0.605(8)	0.3695(3)	0.1401(3)	0.54214(5)	0.41(5)
Si(1′)	0.395				
O(1)	1	0.248(2)	0.943(2)	0.1192(4)	1.5(3)*
O(1′)	1	0.25	0.957(2)	0.375	0.1(2)*
O(1″)	1	0.25	0.947(2)	0.875	0.1(3)*
O(2)	1	0.205(1)	0.476(1)	0.0654(4)	0.4(2)*
O(2′)	1	0.517(1)	0.796(1)	0.0590(3)	0.9(2)*
O(2″)	1	0.322(1)	0.975(1)	0.0515(3)	1.2(2)*
O(2‴)	1	0.020(2)	0.681(1)	0.0560(3)	0.1(2)*
O(3)	1	0.407(1)	0.131(1)	0.9987(5)	1.7(2)*
O(4)	1	0.219(2)	0.213(2)	0.0460(3)	1.3(2)*
O(5)	1	0	0.5	0.1101(4)	1.3(3)*
O(5′)	1	0.5	0	0.1061(4)	0.9(3)*
O(6)	1	0.267(1)	0.734(1)	0.0735(2)	0.5(2)*

Furthermore, since two of these four cations are always Sb(V) one needs only consider the two remaining ones (Si an/or Ge).

An elementary analysis of the various ways to build X_4O_{12} rings from SiO_4 and GeO_4 tetrahedra shows that there are six possibilities schematized as follows:



where ∘ stands for a Si atom and * for a Ge atom. Five of these contain Si atoms; they should lead to five distinct resonance lines but only three, rather broad, peaks are observed (Fig. 3). This suggests that some lines are superimposed and cannot be distinguished by this technique. Now, if one only considers the two nearest neighbor X cations of a Si atom, the six configurations reduce to three distinct ones that could account for the three peaks observed. These three configurations, corresponding to Si atoms with 2, 1, or 0 nearest neighbor Si atoms, can be schematized as follows:



With use of this elementary analysis, a study of the distribution of Si atoms in the various terms of the (Si, Ge) solid solution was undertaken in order to determine whether, as a function of composition, there are certain configurations preferred among the six mentioned above, or if the Si atoms are distributed statistically. A model was developed to calculate the intensity of each peak as a function of composition, similar to that of the successive formation of complexes for which equilibrium constants can be determined. These constants can then be used to evaluate the probability of each configuration. The various possible X_4O_{12} rings are considered as complexes and the equilibria correspond to a progressive substitution of Ge atoms by Si atoms in a Ge_4O_{12} ring. Thus, if [* *; * *] represents the probability of configuration * *; * * in the structure, successive equilibria and their corresponding constants can be written as:

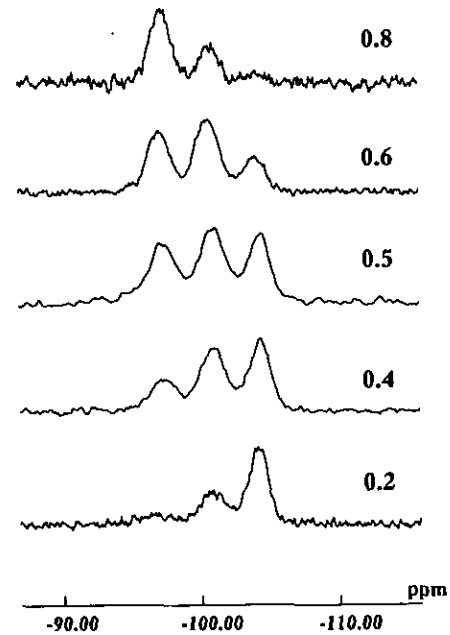


FIG. 3. ^{29}Si MAS NMR spectra for various compositions $Cs_4Sb_4O_8(Si_{4(1-x)}Ge_{4x}O_{12})$ (x values are indicated on the spectra).

TABLE 5
Average <X–O> Distances, X = Si, Ge

Composition	$X(1)O_4$	$X(2)O_4$
$Cs_4Sb_4O_8(Si_4O_{12})$	1.615(8)	
$Cs_4Sb_4O_8[(Si_2Ge_2)O_{12}]$	1.65(4)	1.69(4)
$Cs_4Sb_4O_8[(Si_{8/5}Ge_{12/5})O_{12}]$	1.69(3)	1.70(3)
$Cs_4Sb_4O_8(Ge_4O_{12})$	1.737(6)	1.736(6)

$$\begin{matrix}* & * \\ * & *\end{matrix} + \circ \xleftrightarrow{k_1} \begin{matrix}* & * \\ * & \circ\end{matrix} + * \qquad k_1 = \begin{bmatrix}* & * \\ * & \circ\end{bmatrix} x \Big/ \begin{bmatrix}* & * \\ * & *\end{bmatrix} (1-x)$$

$$\begin{matrix}* & * \\ * & \circ\end{matrix} + \circ \xleftrightarrow{k_2} \begin{matrix}* & * \\ \circ & \circ\end{matrix} + * \qquad k_2 = \begin{bmatrix}* & * \\ \circ & \circ\end{bmatrix} x \Big/ \begin{bmatrix}* & * \\ * & \circ\end{bmatrix} (1-x)$$

$$\begin{matrix}* & * \\ * & \circ\end{matrix} + \circ \xleftrightarrow{k_2'} \begin{matrix}\circ & * \\ * & \circ\end{matrix} + * \qquad k_2' = \begin{bmatrix}\circ & * \\ * & \circ\end{bmatrix} x \Big/ \begin{bmatrix}* & * \\ * & \circ\end{bmatrix} (1-x)$$

$$\begin{matrix}* & * \\ \circ & \circ\end{matrix} + \circ \xleftrightarrow{k_3} \begin{matrix}\circ & * \\ \circ & \circ\end{matrix} + * \qquad k_3 = \begin{bmatrix}\circ & * \\ \circ & \circ\end{bmatrix} x \Big/ \begin{bmatrix}* & * \\ \circ & \circ\end{bmatrix} (1-x)$$

$$\begin{matrix}\circ & * \\ * & \circ\end{matrix} + \circ \xleftrightarrow{k_3'} \begin{matrix}\circ & * \\ \circ & \circ\end{matrix} + * \qquad k_3' = \begin{bmatrix}\circ & * \\ \circ & \circ\end{bmatrix} x \Big/ \begin{bmatrix}\circ & * \\ * & \circ\end{bmatrix} (1-x)$$

$$\begin{matrix}\circ & * \\ \circ & \circ\end{matrix} + \circ \xleftrightarrow{k_4} \begin{matrix}\circ & \circ \\ \circ & \circ\end{matrix} + * \qquad k_4 = \begin{bmatrix}\circ & \circ \\ \circ & \circ\end{bmatrix} x \Big/ \begin{bmatrix}\circ & * \\ \circ & \circ\end{bmatrix} (1-x).$$

All probabilities then appear as functions of both the equilibrium constants and the chemical composition:

$$\begin{bmatrix}* & * \\ * & \circ\end{bmatrix} = k_1 \begin{bmatrix}* & * \\ * & *\end{bmatrix} \frac{1-x}{x}$$

$$\begin{bmatrix}* & * \\ \circ & \circ\end{bmatrix} = k_1 k_2 \begin{bmatrix}* & * \\ * & *\end{bmatrix} \frac{(1-x)^2}{x^2}$$

$$\begin{bmatrix}\circ & * \\ * & \circ\end{bmatrix} = k_1 k_2' \begin{bmatrix}* & * \\ * & *\end{bmatrix} \frac{(1-x)^2}{x^2}$$

$$\begin{bmatrix}\circ & * \\ \circ & \circ\end{bmatrix} = k_1 k_2 k_3 \begin{bmatrix}* & * \\ * & *\end{bmatrix} \frac{(1-x)^3}{x^3}$$

$$\begin{bmatrix}\circ & * \\ \circ & \circ\end{bmatrix} = k_1 k_2' k_3' \begin{bmatrix}* & * \\ * & *\end{bmatrix} \frac{(1-x)^3}{x^3}$$

$$\begin{bmatrix}\circ & \circ \\ \circ & \circ\end{bmatrix} = k_1 k_2 k_3 k_4 \begin{bmatrix}* & * \\ * & *\end{bmatrix} \frac{(1-x)^4}{x^4}$$

$$\begin{bmatrix}* & * \\ * & *\end{bmatrix} = 1 \Big/ \left[1 + k_1 \frac{1-x}{x} + k_1 k_2 \frac{(1-x)^2}{x^2} + k_1 k_2' \frac{(1-x)^2}{x^2} + k_1 k_2 k_3 \frac{(1-x)^3}{x^3} + k_1 k_2 k_3 k_4 \frac{(1-x)^4}{x^4} \right].$$

Hereafter this last expression will be called expression A.

Hypothesis of a Statistical Distribution

In this case of a statistical distribution of Si (and Ge) atoms in the X_4O_{12} rings of the structure, the probability of finding a Ge atom in an XO_4 tetrahedron is the Ge content x and the probability of finding n SiO_4 tetrahedra (and 4-n GeO_4 tetrahedra) in an X_4O_{12} ring is given by the Bernouilli formula, $p_n(x) = C_4^n x^{4-n} (1-x)^n$. The condition $\sum_n p_n(x) = 1$ can then be written in two different ways:

$$\sum_n p_n(x) = C_4^0 x^4 + C_4^1 x^3 (1-x) + C_4^2 x^2 (1-x)^2 + C_4^3 x (1-x)^3 + C_4^4 (1-x)^4$$

$$= C_4^0 x^4 \left[1 + \frac{C_4^1}{C_4^0} \frac{1-x}{x} + \frac{C_4^2}{C_4^0} \left(\frac{1-x}{x} \right)^2 + \frac{C_4^3}{C_4^0} \left(\frac{1-x}{x} \right)^3 + \frac{C_4^4}{C_4^0} \left(\frac{1-x}{x} \right)^4 \right].$$

This last one appears as formally identical to (A) by identifying $C_4^0 x^4$ to $\begin{bmatrix}* & * \\ * & *\end{bmatrix}$, C_4^1/C_4^0 to k_1, C_4^2/C_4^0 to $k_1(k_2 + k_2')$, C_4^3/C_4^0 to $k_1 k_2 k_3$, and C_4^4/C_4^0 to $k_1 k_2 k_3 k_4$.

At this point, it must be mentioned that X_4O_{12} rings with two SiO_4 tetrahedra are divided into two groups that do not contribute in the same way to the intensity of experimental ^{29}Si NMR lines. The following scheme shows that, in the four former configurations, the Si atoms have one nearest-neighbor Si atom, whereas in the latter two they do not have any:

$$\begin{matrix}* & * \\ \circ & \circ\end{matrix} \quad \begin{matrix}\circ & \circ \\ * & *\end{matrix} \quad \begin{matrix}\circ & * \\ * & \circ\end{matrix} \quad \begin{matrix}* & \circ \\ * & \circ\end{matrix} \quad \text{and} \quad \begin{matrix}\circ & * \\ * & \circ\end{matrix} \quad \begin{matrix}* & \circ \\ \circ & *\end{matrix}.$$

Accordingly, the probabilities for these two groups are $p_2(x) = 4x^2(1-x)^2$ and $p_2'(x) = 2x^2(1-x)^2$, respectively.

Equilibrium constants can now be calculated and the following values are obtained:

$$k_1 = 4; \quad k_2 = 1; \quad k_2' = 1/2; \quad k_3 = 1; \quad k_3' = 2; \quad k_4 = 1/4$$

TABLE 6
Configuration Probabilities for Various Ge Contents

x	0	0.2	0.4	0.6	0.8	1
$\begin{bmatrix}\circ & \circ \\ \circ & \circ\end{bmatrix}$	1	0.4096	0.1296	0.0256	0.0016	0
$\begin{bmatrix}\circ & * \\ \circ & \circ\end{bmatrix}$	0	0.4096	0.3456	0.1536	0.0256	0
$\begin{bmatrix}* & * \\ \circ & \circ\end{bmatrix}$	0	0.1024	0.2304	0.2304	0.1024	0
$\begin{bmatrix}\circ & * \\ * & \circ\end{bmatrix}$	0	0.0512	0.1152	0.1152	0.0512	0
$\begin{bmatrix}* & * \\ * & \circ\end{bmatrix}$	0	0.0256	0.1536	0.3456	0.4096	0
$\begin{bmatrix}* & * \\ * & *\end{bmatrix}$	0	0.0016	0.0256	0.1296	0.4096	1

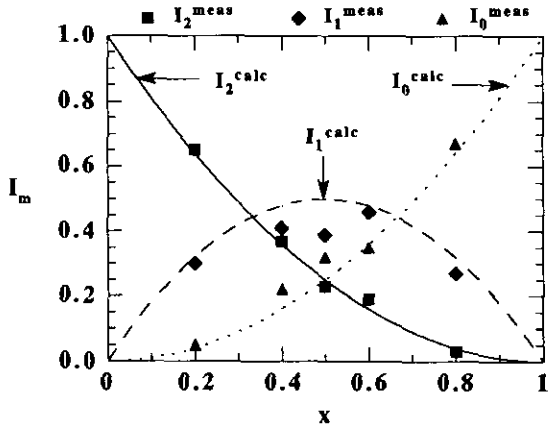


FIG. 4. Calculated and measured intensities (normalized) of the three ^{29}Si NMR peaks as a function of the Ge content x.

With these values the probabilities of the six configurations mentioned above can be determined (Table 6) and the intensity of the three peaks I_m^{calc} corresponding to Si atoms with m nearest neighbor Si atoms (m = 2, 1, or 0) can be calculated:

$$4\begin{bmatrix} \circ & \circ \\ \circ & \circ \end{bmatrix} + \begin{bmatrix} \circ & * \\ \circ & \circ \end{bmatrix} = I_2^{calc} \quad 2\begin{bmatrix} \circ & * \\ \circ & \circ \end{bmatrix} + 2\begin{bmatrix} * & * \\ \circ & \circ \end{bmatrix} = I_1^{calc};$$

$$2\begin{bmatrix} * & \circ \\ \circ & * \end{bmatrix} + \begin{bmatrix} * & * \\ * & \circ \end{bmatrix} = I_0^{calc}.$$

Calculated and measured values of the intensity for the three peaks are plotted in Fig. 4 as a function of the Ge content x. They are in quite fair agreement, thus indicating that the statistical distribution of Si (and Ge) atoms in the X_4O_{12} rings also exists at a local level.

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