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**A complete solid solution between GeO<sub>2</sub> and SiO<sub>2</sub> with the  $\alpha$ -quartz structure: additional X-ray diffraction data from Ge<sub>1-x</sub>Si<sub>x</sub>O<sub>2</sub> flux-grown crystals**

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A complete solid solution between  $\text{GeO}_2$  and  $\text{SiO}_2$  with the  $\alpha$ -quartz structure:  
additional X-ray diffraction data from  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  flux-grown crystals.

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## Abstract

Millimeter-sized crystals of formula  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$ , *i.e.*  $\text{GeO}_2$  materials partially substituted by  $\text{SiO}_2$ , were obtained for the first time both in the middle and the Si-rich parts of the  $\text{GeO}_2$ – $\text{SiO}_2$  composition domain ( $0.5 \leq x \leq 0.93$ ) by spontaneous nucleation using the high-temperature flux method. The X-ray crystal diffraction (XRD) data at room temperature confirm the non-centrosymmetric  $\alpha$ -quartz-type structure and the low level of defects for these as-grown materials. The silicon content in the  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  crystals was determined by interpolation from the inter-tetrahedral bridging angle. The complete mutual solubility is confirmed between  $\alpha$ - $\text{SiO}_2$  and  $\alpha$ - $\text{GeO}_2$ . The deviation from the regularity of the  $\text{TO}_4$  tetrahedra ( $T = \text{Si}, \text{Ge}$ ) decreases linearly when Ge is gradually replaced by Si.

## I. Introduction

The quartz-alpha  $\text{SiO}_2$  ( $P3_121$  or  $P3_221$  space group), with its very precise and very stable oscillation frequencies, is one of the most widely used piezoelectric crystals in the electronics industry for applications as oscillators or in the time-frequency domain. The control of its hydrothermal growth process makes it possible to obtain large and high-quality crystals for industrial uses. However, quartz has a low electromechanical coupling factor  $k_{11}$  of about 9%, and upon heating, it shows a decrease in its properties above  $350^\circ\text{C}$  mainly due to an alpha-beta quartz phase transition at  $573^\circ\text{C}$  [1-3]. To overcome the weakness of quartz in terms of  $k$  and thermal stability,  $\alpha$ -quartz-like materials such as  $\text{GeO}_2$  and  $\text{MXO}_4$  compounds ( $M = \text{B, Al, Ga, Fe, Mn}$ ;  $X = \text{P, As}$ ) have also been studied [4, 5].

Flux-grown germanium dioxide with the  $\alpha$ -quartz structure ( $\alpha\text{-GeO}_2$ ) has a wide operating temperature range under atmospheric pressure until it melts at  $1115^\circ\text{C}$  [6]. At room temperature, this material is largely more efficient than quartz with 3 times higher piezoelectric coefficients [7]. In addition, piezoelectric properties are preserved when the  $\alpha\text{-GeO}_2$  material is subjected to very high temperatures [7, 8]. The strong structural distortion and the meta-stability of the  $\alpha$ -quartz structure of  $\text{GeO}_2$  make it difficult to hydrothermally grow it as large OH-free single crystals OH-free large single-crystals [9]. The high-temperature flux technique has been used successfully to grow  $\alpha\text{-GeO}_2$  single-crystals with high crystalline quality [10]. Nevertheless, there is no industrial production by seeded solution growths of large  $\alpha\text{-GeO}_2$  crystals.

The existence of a solid solution between two pure compounds offers the possibility to adjust the physical properties by adapting the chemical compositions. Several flux-grown mixed compositions are reported in the  $\text{GeO}_2$ -rich part of the  $\text{GeO}_2\text{-SiO}_2$  binary diagram with the low-temperature  $\alpha$ -quartz phase [11, 12]. In addition, non-centrosymmetric mixed crystals

grown hydrothermally have been described in the SiO<sub>2</sub>-rich part [13-15]. Therefore, until now, the growth of  $\alpha$ -quartz-type single crystals with a SiO<sub>2</sub> content between 20 and 80 mol.% has never been reported in the GeO<sub>2</sub>-SiO<sub>2</sub> solid solution.

In the absence of postponed compositions in the middle part of the GeO<sub>2</sub>-SiO<sub>2</sub> binary, a second-order polynomial was used in [11] to fit the evolution with the chemical composition of the ambient lattice parameters  $a$  and  $c$ . Thus, to validate this deviation from Vegard's law, compositions needed to be reported in the middle part of the GeO<sub>2</sub>-SiO<sub>2</sub> binary diagram. The high-temperature flux technique with the spontaneous nucleation method was used in the current work to obtain new mixed Ge<sub>1-x</sub>Si<sub>x</sub>O<sub>2</sub> single-crystals with  $0.5 \leq x \leq 0.93$  and consequently to validate the complete mutual solubility which exists between  $\alpha$ -SiO<sub>2</sub> and  $\alpha$ -GeO<sub>2</sub>.

In this paper, we report the structural results obtained for four crystal compositions from X-ray diffraction (XRD) measurements at room temperature. The effects of the germanium substitution by silicon on the  $\alpha$ -quartz type structure are followed through the variation of structural parameters and angular distortions.

## II. Experimental section

### *Synthesis*

Mixed SiO<sub>2</sub>-GeO<sub>2</sub> single-crystals were grown by spontaneous nucleation in K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub> flux with the use of the slow-cooling growth process. The high-temperature flux method used for growth experiments has already been described in detail elsewhere [12]. In a first step, solutes with 3 different GeO<sub>2</sub>/SiO<sub>2</sub> mole ratios of 1, 0.66, and 0.11 were prepared by heating high purity commercial GeO<sub>2</sub> and SiO<sub>2</sub> powders (99.999% AlfaAesar products) at a very high temperature ( $T > 1400^\circ\text{C}$ ) and then air quenching. Then "solute/flux (K<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>)" mixtures

were prepared with a weight ratio of 10 / 90 whatever the solute composition. For each flux-growth experiment, the 15g-powdered mixture was placed in a Pt crucible covered with a lid, then heated up (150°C/h) to 1020°C, held at this temperature for 24h, then slowly cooled down (5°C/h) to 650°C before turning off the furnace.

For each growth performed in this work, several millimeter-sized transparent and colorless crystals were found trapped in the solidified flux after cooling to room temperature. The crystals were separated from the flux by dissolving the flux in water and they were washed several times with deionized water before their characterization. The reaction yields were of the order of 8 - 10 %.

### ***X-ray diffraction***

An Xcalibur four-circle diffractometer (Oxford diffraction) equipped with both a molybdenum anticathode (monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.71073\text{\AA}$ ) and a CCD detector was used to perform XRD experiments at ambient conditions. As-grown crystals from each experiment were selected by using a stereo microscope equipped with a polarizing filter. Diffraction experiments were performed at room temperature for the best suitable crystals expected to be single crystals. The appropriate software suite CrysAlis [16] was used to handle the collected data and to apply the Lorentz-polarization and absorption corrections to the diffracted intensities.

Structural full-matrix least-squares refinements on  $F^2$  were performed using the SHELX programs [17, 18]. Atomic form factors of neutral atoms extracted from the International Tables for Crystallography were used [19]. Refinements were performed in the trigonal space group  $P3_121$  (n°152) with an atomic Ge/Si mixture at a  $3a$  special site and an oxygen atom at a general site  $6c$ . Anisotropic displacement parameters were considered for all atoms. The resulting atomic positions were standardized using the Structure Tidy program [20].

### III. Results and discussion

The transparent flux-grown mixed  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  materials with  $0.5 \leq x \leq 0.93$  were obtained as individualized colorless crystals. Since these materials result from the partial replacement of germanium by silicon at the same position in the structure, it follows obviously that an increase in their Si content corresponds to a decrease in their Ge content. Four crystals in total were selected for the current diffraction study, one from each of the growth experiments carried out with  $\text{GeO}_2/\text{SiO}_2$  molar ratios of 1 and 0.11 and additionally, two coming from the same experiment with a  $\text{GeO}_2/\text{SiO}_2$  molar ratio of 0.66. This latter choice was intentional to check the homogeneity in composition and the crystalline quality within the material spontaneously grown as crystals. The main information about data collection is provided below in Table I.

The recorded data display the trigonal symmetry which confirms the crystallization of the studied samples with the  $\alpha$ -quartz-type structure. The unit cell contains three units of the formula  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  ( $Z = 3$ ). After careful examination of their diffraction data, three crystals were suspected to be twinned and the corresponding refinements were therefore carried out using TWIN and BASF instructions, which led to a marked improvement in the refinement behavior with a significant decrease in the final agreement factors. The full CIF files are freely available by providing the CSD numbers 2192926 ( $\text{Ge}_{0.07}\text{Si}_{0.93}\text{O}_2$ ), 2192927 ( $\text{Ge}_{0.37}\text{Si}_{0.63}\text{O}_2$ ), 2192928 ( $\text{Ge}_{0.52}\text{Si}_{0.48}\text{O}_2$ ), 2193019 ( $\text{Ge}_{0.39}\text{Si}_{0.61}\text{O}_2$ ) at the Cambridge Crystallographic Data Center [21].

Due to the very small sizes of the crystals, it was not possible to obtain reliable chemical analyses for those selected and used in the diffraction experiments. Alternatively, as already demonstrated in [11], some geometry parameters are useful to estimate with rather good precision the composition of  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  samples having trigonal  $\alpha$ -quartz structures. This is particularly the case of the inter-tetrahedral  $T\text{-O-T}$  angle ( $T = \text{Si}, \text{Ge}$ ) found to vary linearly

with the Si content ( $x$  value) [11]. Note that the Si content is always represented by  $x$  in the formulas but it is also reported in the following as  $x_{\text{Si}}$ , particularly in figures and equations. The bridging angle  $T-O-T$  is the angle formed between two  $TO_4$  tetrahedral vertex-sharing units. This angular parameter does not depend on the Ge to Si ratio but is determined only by the relative position of the peaks (associated with atomic positions) in the electronic density map. According to our previous results [9], the inter tetrahedral  $T-O-T$  angle, measured at  $130.140^\circ$  for  $\alpha\text{-GeO}_2$  and  $143.625^\circ$  for  $\alpha\text{-SiO}_2$ , is assumed to have a linear variation over the entire composition domain in the  $\alpha\text{-GeO}_2\text{-}\alpha\text{-SiO}_2$  pseudo-binary system. Its variation was found to follow the relation:

$$T-O-T (\text{°}) = 13.540 \times x_{\text{Si}} + 130.17 \quad (1)$$

<b>Ge<sub>1-x</sub>Si<sub>x</sub>O<sub>2</sub> formula</b>	<b>Ge<sub>0.52</sub>Si<sub>0.48</sub>O<sub>2</sub></b>	<b>Ge<sub>0.39</sub>Si<sub>0.61</sub>O<sub>2</sub></b>	<b>Ge<sub>0.37</sub>Si<sub>0.63</sub>O<sub>2</sub></b>	<b>Ge<sub>0.07</sub>Si<sub>0.93</sub>O<sub>2</sub></b>
<b>Si content, <math>x_{\text{Si}}</math></b>	0.48	0.61	0.63	0.93
<b>Formula weight, g.mol<sup>-1</sup></b>	83.23	77.44	76.56	63.21
<b>Space group</b>	$P3_121$ (n°152)	$P3_121$ (n°152)	$P3_121$ (n°152)	$P3_121$ (n°152)
<b>Cell dimensions <math>a, c, \text{Å}</math></b>	4.9541(2) 5.5032(3)	4.9451(1) 5.4789(1)	4.9444(2) 5.4754(3)	4.9293(1) 5.4224(1)
<b><math>c/a</math></b>	1.111	1.107	1.107	1.100
<b>Cell volume, <math>\text{Å}^3</math></b>	116.969(10)	116.030(5)	115.924(11)	114.106(5)
<b><math>T-O-T</math> angle, °</b>	136.7(3)	138.7(1)	138.8(1)	142.7(1)
<b><math>d_{\text{calc}}</math>, g.cm<sup>-3</sup></b>	3.545	3.325	3.290	2.759
<b>F(000)</b>	118	111	110	94
<b>Abs. coef. <math>\mu</math>, mm<sup>-1</sup></b>	10.39	8.10	7.74	2.29
<b>Transmission factors</b>	0.32–0.65	0.20–0.37	0.61–0.80	0.74–0.77
<b>Crystal size, <math>\mu\text{m}</math></b>	82×91×183	46×52×107	46×59×93	84×98×108
<b><math>\theta</math> range, °</b>	4.75 – 32.67	3.72 – 32.31	3.72 – 32.30	3.76 – 32.46
<b>Collected/ unique refls</b>	4457 / 277	4514 / 276	4473 / 275	5906 / 273

$R_{int}$	0.0697	0.0215	0.0365	0.0247
$R1 [I > 2\sigma(I)]$	0.0233	0.0101	0.0135	0.0094
$wR_2 [I > 2\sigma(I)]$	0.0622	0.0299	0.0323	0.0242
<b>S</b>	1.348	1.281	1.320	1.207
<b>Extinction coef.</b>	0.034(1)	-	-	0.11(2)
<b>Flack coef.</b>	0.01(5)	-0.007(13)	0.001(17)	0.01(3)
$\Delta\rho$ residuals, e.Å <sup>-3</sup>	0.40 / -0.49	0.29 / -0.35	0.45 / -0.53	0.16 / -0.16
<b>r.m.s. deviation e.Å<sup>-3</sup></b>	0.121	0.075	0.122	0.046

**Table I:** Main crystal data and structural parameters at room temperature for  $Ge_{1-x}Si_xO_2$  crystals ( $T = Si, Ge$ ).  $R_{int} = \sum |F_o^2 - \langle F_o^2 \rangle| / \sum F_o^2$ ,  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$  and,  $S = G.O.F. = [\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$  for  $n$  reflections and  $p$  refined parameters

In the current study, the XRD data processing was performed in two steps according to the procedure already used for flux-grown  $\alpha$ - $Ge_{1-x}Si_xO_2$  single crystals with  $0.021 \leq x \leq 0.18$  in the previous work [11]. So, for each crystal under study, we performed first a series of structural refinements in which the Ge/Si ratio could vary freely. Since Ge and Si are mixed at the same atomic position, the sum of Ge and Si contents is necessarily kept equal to 1 (full site occupation).

The value of the inter-tetrahedral angle  $T-O-T$  which is obtained in such refinement was then used to estimate the Si-content ( $x_{Si}$ ) in the as-grown  $\alpha$ - $Ge_{1-x}Si_xO_2$  crystal. Then, the Ge and Si contents were fixed at their estimated values in a new series of refinements. At the end of each structural refinement, it should be noted that the new  $T-O-T$  angular value does not significantly differ (within the  $3\sigma$  limits) from that formerly used for the evaluation of the chemical composition.

Two  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  samples ( $x = 0.61$  and  $0.63$ ) coming from the same growth experiment with a  $\text{GeO}_2/\text{SiO}_2$  molar ratio solute of 0.66 were characterized to check how similar are the Ge/Si ratios in crystals from a same reaction. From the two crystals under study ( $\text{Ge}_{0.39}\text{Si}_{0.61}\text{O}_2$  and  $\text{Ge}_{0.37}\text{Si}_{0.63}\text{O}_2$ ), the Ge/Si ratio distribution was found close to 5% regarding the accuracy of the method for the chemical determination.

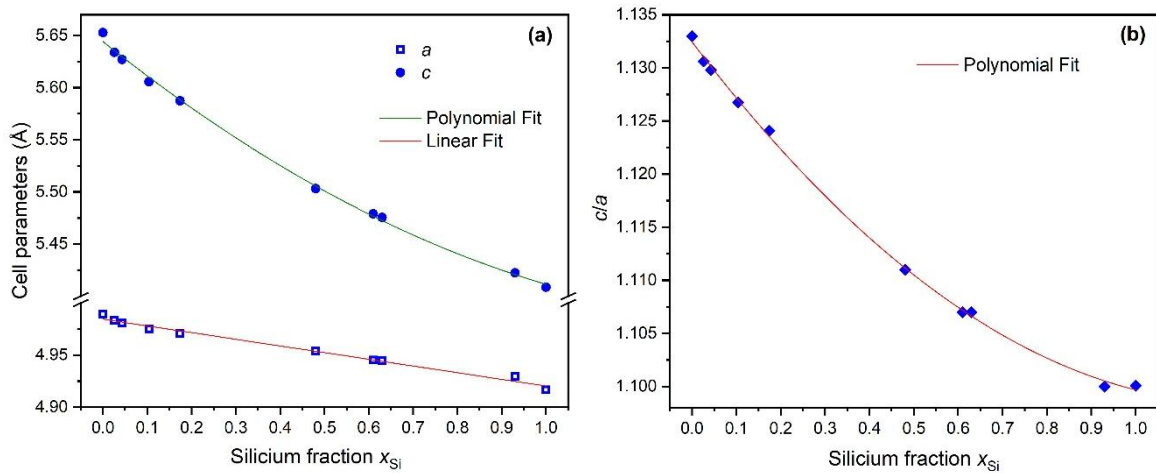
The crystal data and refinement main parameters are reported in Table I for  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  samples with  $x = 0.48, 0.61, 0.63, 0.93$ . The final agreement factors R1, wR2, and S assess the good quality of the structures. The Flack coefficients, which are absolute structure parameters, are refined to values close to zero providing information on the absence of crystalline parts corresponding to the inverse structural model. The atomic fractional coordinates are given in Table II with the equivalent isotropic displacement parameters. The current oxygen coordinates must be transformed by applying the symmetry operation  $(-x, y-x, 1/3-z)$  for direct comparison with positions reported in [11].

<b><math>\text{Ge}_{1-x}\text{Si}_x\text{O}_2</math> formula</b>	<b><math>\text{Ge}_{0.52}\text{Si}_{0.48}\text{O}_2</math></b>	<b><math>\text{Ge}_{0.39}\text{Si}_{0.61}\text{O}_2</math></b>	<b><math>\text{Ge}_{0.37}\text{Si}_{0.63}\text{O}_2</math></b>	<b><math>\text{Ge}_{0.07}\text{Si}_{0.93}\text{O}_2</math></b>
<b>Si content, <math>x_{\text{Si}}</math></b>	0.48	0.61	0.63	0.93
<b><math>T(x_T, 0, \frac{1}{3})</math></b>	0.4583(2)	0.46075(9)	0.46079(11)	0.46749(8)
<b><math>U_{\text{eq } T} (\times 100, \text{\AA}^2)</math></b>	0.136(3)	0.907(11)	0.945(12)	0.769(11)
<b><math>x_{\text{O}}</math></b>	0.4051(9)	0.4086(4)	0.4088(5)	0.4124(3)
<b><math>y_{\text{O}}</math></b>	0.2852(9)	0.2814(4)	0.2811(4)	0.2700(2)
<b><math>z_{\text{O}}</math></b>	0.2294(6)	0.2261(3)	0.1075(3)	0.2169(2)
<b><math>U_{\text{eq } \text{O}} (\times 100, \text{\AA}^2)</math></b>	2.09(7)	1.71(3)	1.80(3)	1.60(2)

**Table II:** Fractional coordinates and equivalent isotropic displacement parameters  $U_{\text{eq}}$  in  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$ . Atoms  $T = \text{Si/Ge}$  are placed at  $3a$  special position  $(x_T, 0, \frac{1}{3})$  and O at  $6c$  general position  $(x_{\text{O}}, y_{\text{O}}, z_{\text{O}})$ .

In the work earlier reported by Lignie et al. [11] for the trigonal  $\alpha\text{-Ge}_{1-x}\text{Si}_x\text{O}_2$  compositions, data was missing in the middle part of the  $\alpha\text{-GeO}_2\text{-}\alpha\text{-SiO}_2$  pseudo-binary system. The new flux-growth syntheses in this solid solution domain have yielded high-quality crystals characterized in the current work by non-centrosymmetric trigonal symmetry. Consequently, new crystallographic data are now available (Table I) to complete the sampling in the solid solution  $\alpha\text{-GeO}_2\text{-}\alpha\text{-SiO}_2$  and provide for the first time real proof of the continuity of this solid solution over its entire composition domain.

The evolution of both the experimental lattice parameters at room temperature and the  $c/a$  ratio is plotted as a function of the Si-content  $x_{\text{Si}}$  in Figure 1. The ambient cell parameters for the terminal members,  $\alpha\text{-GeO}_2$  and  $\alpha\text{-SiO}_2$  are taken from the previous work, as well as for the  $\text{GeO}_2$ -rich flux-grown  $\alpha\text{-Ge}_{1-x}\text{Si}_x\text{O}_2$  compositions with  $0.021 \leq x \leq 0.18$ , [11].



**Figure 1:** Evolution of (a) unit cell parameters  $a$  and  $c$  and (b)  $c/a$  ratio with the silicon content in  $\alpha\text{-Ge}_{1-x}\text{Si}_x\text{O}_2$ . Solid lines are fitting curves of the experimental data. Error bars are smaller than the symbol size. Data for  $x_{\text{Si}} = 0, 0.026, 0.043, 0.104, 0.174, 1$  are taken from [11].

As the substitution of Ge by Si increases, the cell parameters  $a$ ,  $c$ , and the  $c/a$  ratio are found to decrease, which corresponds to a reduction in the cell volume, Table I and Fig. 1. The

progressive replacement in the structure of  $\alpha\text{-Ge}_{1-x}\text{Si}_x\text{O}_2$  of the Ge atoms by Si atoms affects the lattice constants and it is not unexpected as Si is a smaller element than Ge. As these elements are present as cations in this structure, it is relevant to compare their ionic radii and to observe that the ionic radius of  $\text{Si}^{4+}$  is about 32% smaller than that of  $\text{Ge}^{4+}$ .

Over the whole  $\text{GeO}_2\text{-SiO}_2$  solid solution range, the behavior of parameter  $c$  was fitted to a second-degree polynomial, Fig. 1(a). When considering a second-order polynomial fit for parameter  $a$ , the second-order term is found extremely small and therefore the linear fit given below is more relevant.

$$a \text{ (\AA)} = -0.064 \times x_{\text{Si}} + 4.980 \quad (2)$$

$$c \text{ (\AA)} = 0.107 \times x_{\text{Si}}^2 - 0.341 \times x_{\text{Si}} + 5.640 \quad (3)$$

A second-order polynomial was the best to fit the behavior of the  $c/a$  value as a function of the Si content in the  $\text{GeO}_2\text{-SiO}_2$  system, Fig. 1(b):

$$c/a = 0.022 \times x_{\text{Si}}^2 - 0.055 \times x_{\text{Si}} + 1.133 \quad (4)$$

The  $c$  parameter and therefore the  $c/a$  ratio for crystals with the  $\alpha$ -quartz structure in the  $\text{GeO}_2\text{-SiO}_2$  pseudo-binary system does not follow Vegard's law (Fig. 1). The deviation from Vegard's law for these two parameters was already reported in a previous paper where both the  $a$  and  $c$  experimental cell parameters were fitted with a second-order polynomial [11]. The addition of new data for some compositions  $\alpha\text{-Ge}_{1-x}\text{Si}_x\text{O}_2$  in the middle range, now, permits consideration of a linear variation with the Si-content for the parameter  $a$  in the solid solution  $\text{GeO}_2\text{-SiO}_2$ . In contrast, the variation of parameter  $c$  is still well-fitted with a second-order polynomial. Based on the present characteristics, it is confirmed that the volume contraction

with increasing the Si fraction occurs preferentially along the polar  $c$ -axis, as stated earlier [11].

Also interesting are the variations with the Si content of the inter-atomic distances  $T-O$  and the intra-tetrahedral angles  $O-T-O$  ( $T = \text{Si, Ge}$ ). As there are four  $T-O$  bonds in a tetrahedron, there are therefore 6 intra-tetrahedral angles. These bond lengths and angular values are listed in Table III for the four Si/Ge mixed compositions under study. The  $T-O$  bond length decreases as the Si content increases in good agreement with the drastic reduction in the ionic radius (also atomic radius decrease) when going from Ge to Si. This is well illustrated in Figure 2 with the variation of the average bond lengths values  $\langle T-O \rangle$  drawn as a function of the Si content,  $x_{\text{Si}}$ , for various compositions of the germanium-silicon oxides  $\alpha\text{-Ge}_{1-x}\text{Si}_x\text{O}_2$ .

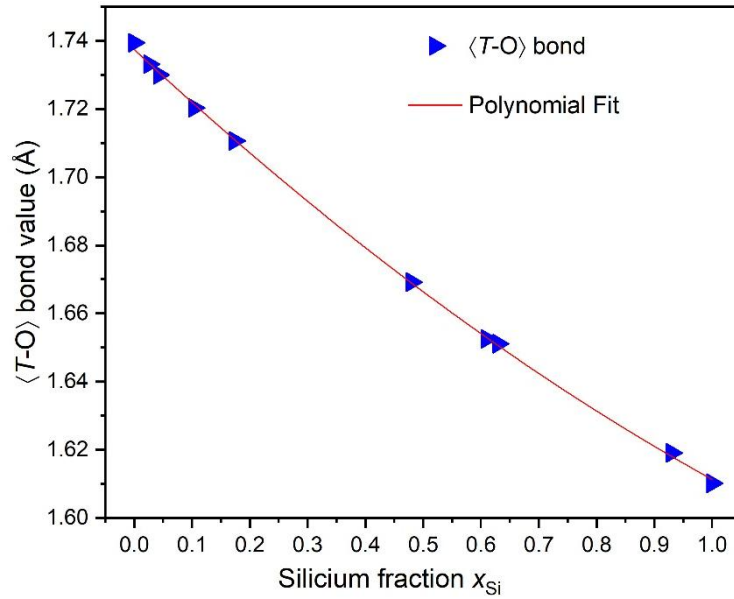
<b><math>\text{Ge}_{1-x}\text{Si}_x\text{O}_2</math> formula</b>	<b><math>\text{Ge}_{0.52}\text{Si}_{0.48}\text{O}_2</math></b>	<b><math>\text{Ge}_{0.39}\text{Si}_{0.61}\text{O}_2</math></b>	<b><math>\text{Ge}_{0.37}\text{Si}_{0.63}\text{O}_2</math></b>	<b><math>\text{Ge}_{0.07}\text{Si}_{0.93}\text{O}_2</math></b>
<b>Si content, <math>x_{\text{Si}}</math></b>	0.48	0.61	0.63	0.93
<b><math>T-O</math> bond</b>	$2 \times 1.663(4)$ $2 \times 1.675(3)$	$2 \times 1.645(2)$ $2 \times 1.660(2)$	$2 \times 1.644(2)$ $2 \times 1.658(2)$	$2 \times 1.614(1)$ $2 \times 1.626(1)$
<b><math>\langle T-O \rangle</math> mean bond</b>	1.6692	1.6525	1.6511	1.6197
<b>d.i. (T-O)</b>	0.0019	0.0022	0.0022	0.0018
<b><math>O-T-O</math> angles</b>	107.8(1) 107.8(1) 108.6(3) 108.9(3) 111.9(2) 111.9(2)	108.0(1) 108.0(1) 109.1(1) 109.3(1) 111.2(1) 111.2(1)	108.1(1) 108.1(1) 109.2(1) 109.2(1) 111.2(1) 111.2(1)	108.7(1) 108.7(1) 109.0(1) 109.1(1) 110.6(1) 110.6(1)
<b><math>\langle O-T-O \rangle</math> mean angle</b>	109.48	109.46	109.48	109.48

$d.i. (O-T-O)$	0.0145	0.0107	0.0103	0.0071
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**Table III:**  $T-O$  bond lengths ( $\text{\AA}$ ) and  $O-T-O$  intra-tetrahedron angles ( $^\circ$ ) ( $T = \text{Si, Ge}$ ). The associated distortion indices are defined as  $d.i. = \sum_{i=1}^n |y_i - \langle y \rangle| / (n \times \langle y \rangle)$  where  $y_i$  and  $\langle y \rangle$  are the individual and average values of tetrahedral bond lengths or intra-tetrahedral angles [11]. Standard deviations are given in parentheses.

A second-order polynomial fit of the  $\langle T-O \rangle$  experimental average values  $\langle T-O \rangle$  gives the following equation:

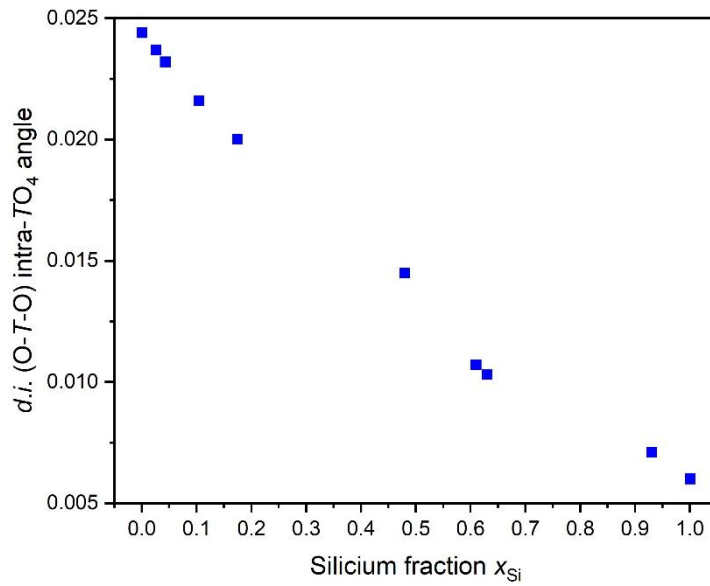
$$\langle T-O \rangle (\text{\AA}) = 0.032 \times x_{\text{Si}}^2 - 0.158 \times x_{\text{Si}} + 1.737 \quad (5)$$



**Figure 2:** Evolution of  $\langle T-O \rangle$ , the average value of  $T-O$  bond lengths, with the Si content. Data for  $x_{\text{Si}} = 0, 0.026, 0.043, 0.104, 0.174, 1$  are taken from [11]. Solid line represents the second-order least squares fit. The error bars are smaller than the symbol size.

To follow the structural changes along with the substitution rate, it is instructive to look at the distortion indices calculated for the  $T-O$  bond lengths and for the  $O-T-O$  intra-tetrahedral angles. The distortion index is a parameter that gives an evaluation of the deviation of

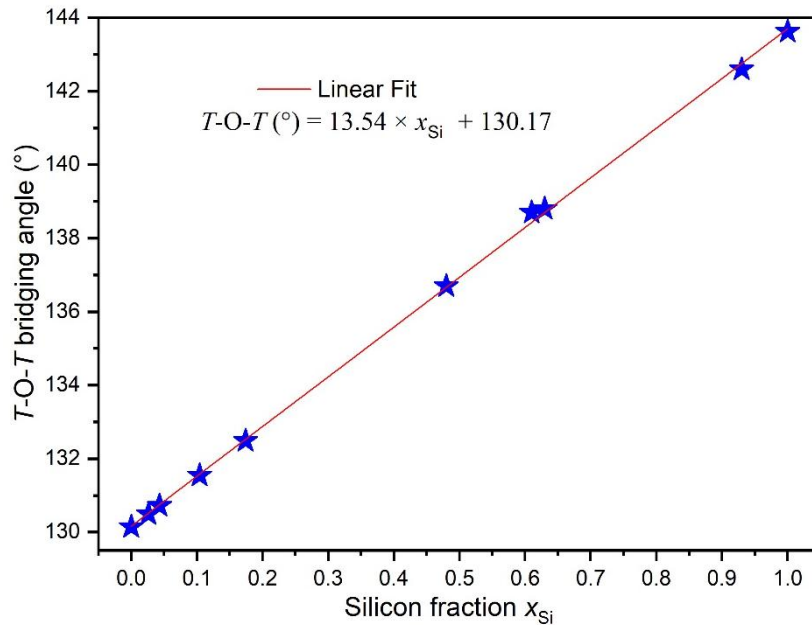
individual parameters to their mean value. Note that only slight changes occur in the distortion indices (*d.i.*) corresponding to the  $T$ -O distances in  $TO_4$  tetrahedra when passing from  $\alpha$ -GeO<sub>2</sub> to  $\alpha$ -SiO<sub>2</sub>. This indicates that changing the nature of the  $T$  atom does not produce bond length dispersion in the tetrahedra  $TO_4$ , which is normal as only one crystallographic site is concerned and substitution is done homogeneously at all the tetrahedron vertices such as the four bond lengths vary together.



**Figure 3:** Evolution of the distortion indices for intra-tetrahedral O– $T$ –O angles with the Si-content. Data for  $x_{Si} = 0, 0.026, 0.043, 0.104, 0.174, 1$  are taken from [11]. Error bars are smaller than the symbol size. Distortion indices are defined as  $(\sum_{i=1}^n |y_i - \langle y \rangle|) / (n * \langle y \rangle)$  with  $y_i$  the individual and  $\langle y \rangle$  the mean intra-tetrahedral angles [9].

Instead, a great decrease is noted for the intra-tetrahedral angular distortion indices *d.i.* (O– $T$ –O) as reported in Table III and Fig. 3. This parameter is representative of the O– $T$ –O angles ability to approach the ideal value of  $109.5^\circ$  which is characteristic of a regular tetrahedron. Its variation brings a good image of the trend for the  $TO_4$  tetrahedra described in the  $P3_121$  space group with symmetry 3 to gradually approach the symmetry  $T_d$  as the Si content increases.

In the  $TO_2$  family ( $T = \text{Si}, \text{Ge}$ ), the  $\alpha$ -quartz-type trigonal structure is composed of  $TO_4$  tetrahedra, each sharing two vertices with alike units. Thus, variations in the intra-tetrahedral angles also result in correlated changes in the inter-tetrahedral bridging angles  $T-O-T$ . The reduction of the  $TO_4$  tetrahedra distortion, associated with the diminution of *d.i.* ( $O-T-O$ ) when the Si content increases in these mixed-growth compounds, Fig. 3, marks the tendency for the  $TO_4$  units to approach the tetrahedral symmetry. This is made possible by the simultaneous decrease in the  $O-T-O$  intra-tetrahedral angles, Table III, and the  $c/a$  ratio, Fig. 1(b), along with the increase in the bridging  $T-O-T$  angles, Fig. 4.



**Figure 4:** Evolution of the bridging  $T-O-T$  angle between  $TO_4$  units with the Si content. Data for  $x_{\text{Si}} = 0, 0.026, 0.043, 0.104, 0.174, 1$  come from [11]. Error bars are smaller than the symbol size.

#### IV. Conclusion

In the present study, a suitable method and appropriate conditions have been found for the spontaneous growth of millimeter-sized OH-free  $\text{Ge}_{1-x}\text{Si}_x\text{O}_2$  single crystals with  $0.5 \leq x \leq 0.93$ . The new compositions reported here for high-quality flux-grown crystals having the

non-centrosymmetric  $\alpha$ -quartz trigonal structure lead to provide, for the first time, a complete assessment of the  $\text{GeO}_2\text{-SiO}_2$  solid solution. The silicon fraction was determined using the linear relationship established for the inter-tetrahedral bridging angle. Except for the bridging  $T\text{-O-T}$  angle, the main structural parameters such as cell dimensions, characteristic bonds and angles deviate from the Vegard law when germanium is gradually replaced by silicon, in conjunction with a higher distortion of the  $\alpha$ -quartz  $\text{GeO}_2$  compared to the more regular  $\alpha\text{-SiO}_2$  structure. The existence of a complete and continuous solid solution  $\alpha\text{-GeO}_2\text{-}\alpha\text{-SiO}_2$  suggests that piezoelectric, optic, elastic, and mechanical properties are readily tunable by adjusting the Si and Ge contents at the mixed atomic site.

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