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The crystal lattice thermal expansion of an oxynitride glass–ceramic material of high-quartz structure

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An N^{3-} for O^{2-} substituted oxynitride high-quartz material of essentially 1 : 1 : 2 β-eucryptite composition was prepared and the effect of the nitrogen substitution on the thermal expansion of the crystal lattice studied. The substituted material of ~5.8 anion % nitrogen is isostructural with β-eucryptite. The thermal expansion behaviour of the oxynitride crystal lattice is similar to that of the β-eucryptite lattice, but a drastic decrease in expansion anisotropy is noted.

1. Introduction

Work at Corning Glass Works and elsewhere [1–5] has shown that in silicate glasses, part of the oxygen can be replaced by nitrogen. The published literature showed that nitrogen substitution increases the viscosity, the refractive index, the density, and the stability of the glasses studied.

These observations may be explained by the following model. The oxygen ion (O^{2-}) is normally 2-connected in most silicates, while the nitrogen ion (N^{3-}) is normally 3-connected. In Si_3N_4, for example, three SiN_4 tetrahedra share a corner. In Si_2N_2O, the oxygens are 2-connected, the nitrogens 3-connected, in accordance with the above connecting schemes. Assuming this to be the normal state of affairs, we can expect the observed increases in the density and viscosity of a given oxide glass when we substitute nitrogen for part of the oxygens.

If we suppose this reasoning to be essentially correct, it becomes interesting to try to answer the question: Are similar effects on the properties of a crystalline silicate material observed when we replace part of the oxygen by nitrogen? β-eucryptite ($Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$) was chosen as the material to provide an answer to that question, because β-eucryptite is easily prepared, the crystal structure and lattice parameters are well known, and its materials properties are well established.

This paper is concerned with one of the properties of β-eucryptite and changes in that property with N^{3-} for O^{2-} substitution, namely the crystal lattice thermal expansion, which is usually very responsive to minute chemical changes. The axial thermal expansions of β-eucryptite are well documented [6–8].

β-eucryptite is of a high-quartz or β-quartz type crystal structure (space group $P6_222$) with half of the Si^{4+} ions replaced by Al^{3+}, and the charge balance maintained by Li^+ ions. It is usually referred to as a lithium-stuffed quartz, where the high-quartz structure has been retained after crystallization due to the lithium stuffing.

The thermal expansion of the crystal lattice of β-eucryptite is highly anisotropic with the *a*-unit cell axis linearly expanding and the *c*-axis linearly contracting upon heating. Even slight changes in this expansion behaviour, if discovered in the case under study, will be indicative of structural effects caused by the anion substitution of N^{3-} for O^{2-}.

2. Experimental procedure

2.1. Sample preparation

The composition of the glass used for the

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TABLE I Batched and analysed composition of oxynitride ceramic

Component	Mole ratio	
	Batched	Analysed*
Li_2O (as Li_2CO_3)	1.0	1.0
Al_2O_3	1.0	1.05
SiO_2	1.16	1.86
$\frac{1}{3}Si_3N_4 = SiN_{4/3}$	0.84	0.14†

*Approximate stoichiometry = $Li_2Al_2Si_2O_{7.32}N_{0.45}$ with anion % = [N]/{[0] + [N]} × 100 = 5.8.

†There was considerable loss of nitrogen during melting.

preparation of the β-eucryptite oxynitride glass–ceramic is given in Table I. The glass was prepared by melting the blended batch materials in a molybdenum crucible in nitrogen gas atmosphere at 1650° C for 6 h. The melt was poured into a patty and crytallized under nitrogen at 800° C for 2 h and subsequently at 1000° C for an additional 2 h. The chemical analysis of the crystallized material is given in the table. The nitrogen content was measured using a Leko TN-15 Nitrogen Determinator. The sample was ground to −325 mesh for the powder X-ray diffraction work.

For simplicity, the regular oxygen β-eucryptite will be referred to as β-eucryptite (O) and nitrogen containing β-eucryptite as β-eucryptite (N).

2.2. Instrumental details

The room temperature powder X-ray diffraction work was performed on a Norelco wide angle diffractometer–generator combination with a Canberra electronics panel and proportional counter. Reflected beam monochromatized copper radiation was utilized to strip chart record the X-ray diffraction pattern of the nitride glass–ceramic.

A UNICAM S-150 high temperature powder camera was employed for the X-ray thermal expansion studies. The use of this camera eliminates the need for an internal standard material because of built-in fiducial markers of known angular positions and allows the use of a split-film technique which is based on the recording of two diffraction patterns at different sample temperatures on the same film, and holds all errors constant [9, 10].

The powdered specimens were mounted in 0.3 mm fused quartz capillaries, and the diffraction patterns, as a function of sample temperature up to about 800° C, were split-film recorded with nickel-filtered copper radiation.

2.3. Data evaluation

To determine the crystal lattice thermal expansion of a material means monitoring of the angular positions of suitable X-ray reflections in the diffraction patterns of that material as a function of sample temperature, and to calculate the lattic parameters from those reflections for the various temperatures. Most suitable for that purpose are diffracted lines whose Miller indices are such that their angular positions are influenced only by the magnitude and/or changes in magnitude of one unit cell axis. In the hexagonal system, for instance, lines of *hk*0 indices permit the calculation of the *a* parameter directly, and 0 0 *l* lines the calculation of *c*. Lines of this nature are not always present in a diffraction pattern, and lines where $h^2 + k^2 + hk \gg l^2$ and $l^2 \gg h^2 + k^2 + hk$ can be used to calculate *a* and *c*, respectively, from two equations in two unknowns. It is also desirable to work with lines of the highest observable angle of reflection because intrinsic and systematic errors decrease with increasing angle.

The X-ray diffraction pattern of the β-eucryptite (N), as is typical for most glass–ceramics, shows lines of appreciable intensity only in the low angle region. The uniquely indexed lines present in the diffraction pattern, their Miller indices, spacings (*d*) and angle of reflection (2*θ*), are listed in Table II. Column 4 of the table indicates the weighted influence of the lattice parameters *a* and *c* on the angular positions of the lines listed. It can be seen that two lines, 2 0 0 and 2 2 0, are influenced in their position only by the magnitude of the *a*-axis. Changes in that magnitude with changes in temperature can therefore be determined directly

TABLE II Usable reflections in X-ray diffraction pattern of β-eucryptite (N)

hlk	*d* (nm)	2*θ* (deg)	Weighting (*a* : *c*)
2 0 0	0.228	39.5	a^2
1 1 2	0.191	47.7	$4a^2 : 4c^2$
2 1 1	0.164	55.9	$\sim 9a^2 : c^2$
2 0 3	0.143	65.1	$\sim 5a^2 : 9c^2$
3 0 2	0.133	70.8	$12a^2 : 4c^2$
2 2 0	0.132	71.8	a^2

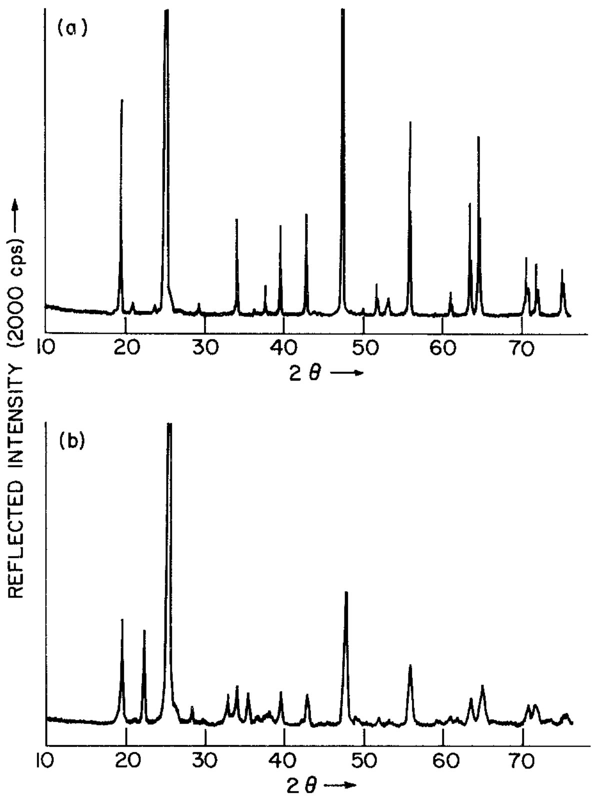

Figure 1 X-ray diffraction pattern of (a) oxygen β-eucryptite (O); (b) oxynitride β-eucryptite (N).

from these lines, i.e. from the 2 2 0 line which is of highest angle, and the 2 0 0 reflection can be used to confirm the trends found in the a-axis thermal expansion.

There is only one line in Table II that is predominantly influenced in its position by the c-axis and changes in the length of that axis, the 2 0 3 reflection. Once a is known, c can be calculated from the d_{203} spacing as

$$c = 3\Big/\left(\frac{1}{d_{203}^2} - \frac{16}{3a^2}\right)^{\frac{1}{2}} \qquad (1)$$

Using this strategy, we can obtain the lengths of the a and c lattice parameters and changes in those lengths with variations in sample temperature.

Using the a and c values calculated for various temperatures, we can check our results for internal consistency by calculating the theoretical d-spacings for the 1 1 2 reflection, which is equally weighted by a^2 and c^2, from these a and c values, and compare these theoretical spacings with the observed ones. The spacing d_{112} can be calculated by the general equation

$$d_{hkl} = \frac{ac\sqrt{3}}{[4(h^2 + k^2 + hk)c^2 + 3l^2a^2]^{\frac{1}{2}}} \qquad (2)$$

or

$$d_{112} = \frac{ac\sqrt{3}}{[12(c^2 + a^2)]^{\frac{1}{2}}} \qquad (3)$$

If these calculated d values agree with the observed values within the estimated errors of the method employed, we are satisfied that our axial expansions are correct as calculated.

3. Results and discussion

A chemical analysis of the β-eucryptite (N) glass–ceramic was performed. The results are summarized in Table I, and show that the specimen does indeed contain nitrogen in the bulk material. If one takes the oxygen equivalent of the 2.51 wt % nitrogen, and assumes the latter to be distributed uniformly throughout the bulk of the material, one calculates a mole ratio of almost exactly 1 : 1 : 2 for the nitrogen containing β-eucryptite phase with part of the oxygen replaced by nitrogen.

The room temperature X-ray diffraction pattern of the β-eucryptite (N) glass–ceramic and of the 1 : 1 : 2 β-eucryptite (O) are shown in Fig. 1. Comparison of the traces shows that both are very similar, indicating that β-eucryptite (N) is

TABLE III Precision lattice parameters of glass–ceramics β-eucryptite (N) and β-eucryptite (O)

	β-Eucryptite (N)	β-Eucryptite (O)
a(nm)	0.5262	0.5248
c(nm)	0.5530	0.5593
c/a	0.105	0.107
V(nm^3)	0.132 59	0.133 40

indeed of a high-quartz crystal structure. No evidence for the presence of a glassy phase in the material under study was detected. A few additional lines observed in the pattern of the β-eucryptite (N) indicate the presence of an additional minor crystalline phase, a fact confirmed by TEM observations. The additional lines can be matched by those of α-cristobalite.* Systematic shifts in the positions of these lines may be indicative of the fact that N → O substitution has taken place here too. This is, however, of no interest for the purposes of this paper, which is concerned with the thermal expansion of nitrogen substituted β-eucryptite. No attempt was therefore made to confirm or disprove the presence of nitrogen in this minor phase. Another feature to be noted in Fig. 1 is the overall decrease in reflected intensity in the X-ray pattern of β-eucryptite (N), and the further decrease in intensity with increasing angle of reflection. These decreases in intensity, when compared to the pattern of the stoichiometric β-eucryptite (O)†, show that in the case of β-eucryptite (N), we are dealing with a β-eucryptite phase that is intrinsically less ordered and contains probably more glass than the better crystallized β-eucryptite (O) specimen.

The room temperature lattice parameters of the β-eucryptite (N) phase are given in Table III, together with those of β-eucryptite (O). One sees that an increase in the length of the a parameter and a decrease in the c parameter are found in the case of the nitrogen for oxygen substitution. Are these changes in the lattice parameters actually the results of the anion substitution, or could they instead be caused by a simple change in the mole ratios of $Li_2O : Al_2O_3 : 2SiO_2$, i.e. one of the high-quartz types known to crystallize up to a ratio of about 1 : 1 : 3.5? The answer to the first part of the question is yes, we are justified in assuming these changes to be the result of the anion substitution because, for simple compositional changes from 1 : 1 : 2 to 1 : 1 : 3.5, the a-axis remains of constant length while the c-axis decreases more sharply than is observed here. We can, therefore, determine the crystal lattice thermal expansion of the β-eucryptite (N) material assuming a high-quartz crystal structure.

TABLE IV Lattice parameters at elevated temperatures of high-quartz phase in glass–ceramic β-eucryptite (N)

Temperature (° C)	a (nm)	c (nm)	V (nm^3)
22	0.526 19	0.552 97	0.132 59
200	0.526 69	0.552 50	0.132 73
400	0.527 24	0.551 99	0.132 89
600	0.527 81	0.551 47	0.133 05
800	0.528 37	0.550 95	0.133 20

The results of the calculations of the lattice parameter of the β-eucryptite (N) high-quartz phase as a function of sample temperature are summarized in Table IV in steps of 200° C up to 800° C. The axial thermal expansions of the two high-quartz crystal lattices and the linear thermal expansion of the two specimens, calculated from the former, are plotted in Fig. 2, in ppm.

One sees that the axial thermal expansions of the β-eucryptite (N) material are anisotropic with the a-axis expanding linearly upon heating, and the c-axis contracting linearly throughout the temperature range from 22 to 800° C. This expansion behaviour is similar to the expansion of the crystal lattice of β-eucryptite (O) and confirms once more the assumed structural similarity. The magnitudes of the positive and negative axial expansions are, however, much smaller in the case of the β-eucryptite (N) material than those of the β-eucryptite (O).

Fig. 2 shows that the negative expansion of the crystal lattice of β-eucryptite (N) parallel to the c-axis is less by a factor of 4 when compared to β-eucryptite (O), while the positive expansion perpendicular to the c-axis has decreased by about one-third. The combined effect of these axial expansions on the calculated linear expansion is an increase in the case of β-eucryptite (N)

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*JCPDS card no. 11-695.

†The 1 : 1 : 2 β-eucryptite (O) was melted from a stoichiometric mixture of milled African sand, reagent grade Al_2O_3, and reagent grade Li_2O_3, at 1650° C for 16 h, and subsequently ground and crystallized at 1000° C for 6 h.

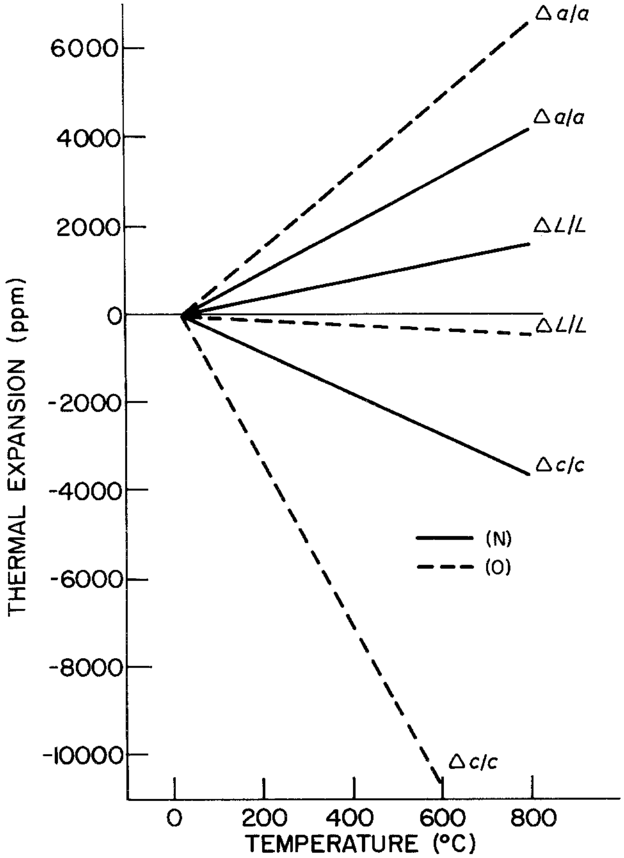

Figure 2 Crystal lattice and calculated linear thermal expansions of (N) oxynitride β-eucryptite (O) oxide β-eucryptite.

to a positive value of about 1600 ppm at 800° C, while the axial expansions of β-eucryptite (O) lead to a slightly negative value of approximately -550 ppm at the same temperature.

The axial thermal expansion coefficients and the calculated coefficient of the linear thermal expansion of the high-quartz phase β-eucryptite (N), and of the 1 : 1 : 2 β-eucryptite (O) material, are summarized in Table V. It is not the purpose of this paper to appraise β-eucryptite (N) high-quartz as a material from an expansion point of view, but it should be noted in passing that the considerably lowered anisotropy would make it a material of more interest than β-eucryptite (O), especially if one assumes that varying degrees of anion substitution might lead to different expansion behaviour of the crystal lattice.

4. Conclusion

It has been shown by chemical analysis that anion substitution of N^{3-} for O^{2-} can be accomplished in a crystalline silicate, in this case in an approximately 1 : 1 : 2 β-eucryptite. The resulting materials can be expected to have properties different from those of non-substituted silicates. In the example studied, a 2.5% nitrogen-containing specimen, it was found by X-ray diffraction and high temperature X-ray diffraction that an oxynitride eucryptite material retained the high-quartz structure of the oxygen eucryptite, and has different lattice parameters. The thermal expansion behaviour of the new crystal lattice confirms that the material is isostructural with the oxygen β-eucryptite. The *a*-axis expands linearly upon heating and the *c*-axis contracts. The major effect of the anion substitution was found to be on the expansion anisotropy which is much lower in the case of the nitrogen substituted material.

TABLE V Axial and calculated linear thermal expansion coefficients of β-eucryptites

	β-Eucryptite (N) (22 to 800° C)	β-Eucryptite (O) (22 to 743° C)
$\alpha_a (10^6\,°C^{-1})$	5.3	8.03
$a_c (10^6\,°C^{-1})$	4.7	-17.05
$\alpha (10^6\,°C^{-1})$	2.0	-0.38

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