

Volume expansion during reaction sintering of γ -Bi₁₂SiO₂₀

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Abstract

Preparation of γ -Bi₁₂SiO₂₀ from a compacted mixture of α -Bi₂O₃ and SiO₂ powders is described. A very large volume expansion, related to the phase formation, is observed during heat treatment at 600°C. It is shown that the dedensification results from a preferential diffusion of bismuth and oxygen ions towards SiO₂, through the layer of γ -Bi₁₂SiO₂₀ which forms around a silica grain. The expansion begins when γ -Bi₁₂SiO₂₀ grains form a continuous skeleton. When bismuth oxide grains are isolated in the skeleton, expansion and reaction rates are proportional. A quantitative model is proposed to describe this situation assuming an isotropic matter transfer and no coalescence between the γ -Bi₁₂SiO₂₀ grains. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

γ -Bi₁₂SiO₂₀ (BSO), like γ -Bi₁₂GeO₂₀ (BGO), is used in numerous photorefractive devices. Such applications mainly concern single crystals^{1–3} and thin films.^{4,5} As the presence of grain boundaries in polycrystals is supposed to affect drastically the electro-optic properties, the preparation of BSO ceramics has generally been neglected.

Besides the usual route, which consists first in synthesizing the BSO powder and then in sintering the product after grinding, a process involving reaction and densification during the same heat treatment may have some interest. Its efficiency is strongly dependent on the matter and pore transport during the reaction step. A typical dilatometric curve of such a reaction sintering process is given in Fig. 1. A large volume expansion occurs between 610 and 710°C. The purpose of this paper is to describe the matter transfer which is responsible for this dedensification.

2. Mixture preparation and treatment conditions

The starting materials are monoclinic α -Bi₂O₃ (Johnson Matthey, purity 99.9995%) and hexagonal SiO₂ (Aldrich, purity 99.6%) commercial powders. To eliminate traces of carbonates⁶ and sorbed species, α -Bi₂O₃ and SiO₂ are

first heat treated, respectively, at 400°C for 8 h and at 1000°C for 2 h. Both calcined powders are weighed in stoichiometric proportions and mixed in ethanol by attrition for 4 h, using zirconia balls. Phosphate ester (Beycostat C213, CECA) is used as a dispersant, to avoid phase segregation during mixing. Liquid is then removed at 50°C using a primary vacuum, in a rotating evaporator.

The specific surface area, determined by the BET method (Flowsorb 2300 II Micromeritics) after a 2 h treatment at 110°C, is 2.0 m² g⁻¹. X-ray diffraction patterns of the mixture exhibit only the characteristic peaks of α -Bi₂O₃. SiO₂ is not detected, probably due to its low concentration (7 vol%). Therefore, there is no apparent mechanical-synthesis of BSO during ball-milling, contrary to that was observed for BGO.⁷

The dry mixture is granulated in a 125 μ m sieve. Then the granulates are die pressed at 12.5 MPa, into 10 mm diameter pellets (about 0.8 g). The apparent density of as-obtained compacts, determined from geometrical measurements, is 5.0 g cm⁻³.

Samples, placed on a gold boat, are heated at 6°C min⁻¹, up to the holding temperature. Based on the results reported in Fig. 1, isothermal treatments are performed at 600°C, in order to slow down the kinetics of expansion. After a holding time ranging from 0 to 1200 min, the ceramics are quenched in air. Whatever the holding time, samples exhibit a 1% mass loss corresponding to the removal of the dispersant.

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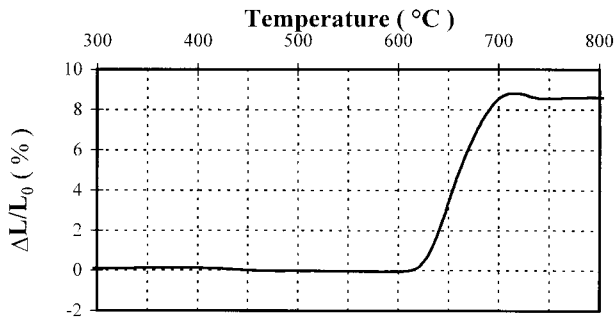


Fig. 1. Evolution, versus temperature, of the relative dimension of a 6 α - Bi_2O_3 1 SiO_2 compact mixture. Initial apparent density: 5.0 g cm^{-3} , heating rate: 5°C min^{-1} .

3. Characterization

The expansion of the compacts and their relative density are determined from geometrical measurements of the sample dimensions. The estimated accuracy is 0.5% and 1.5%, respectively.

The progress of the reaction between Bi_2O_3 and SiO_2 are followed by X-ray diffraction using a Debye-Scherrer camera equipped with a curved position sensitive detector (INEL CPS 120) and a forward monochromator selecting the $\text{CuK}\alpha_1$ radiation. All experiments are done with an incidence angle fixed to 10° . After heat treatment, samples are hand-ground in an agate mortar, to obtain elementary particles with a size small enough to ensure the statistical character of the information. To determine the relative amount of each crystallized phase, an abacus is made using the following procedure:

- (i) pure γ - $\text{Bi}_{12}\text{SiO}_{20}$ is prepared by heat treating compacts at 800°C for 8 h and hand-grinding;
- (ii) γ - $\text{Bi}_{12}\text{SiO}_{20}$ and commercial α - Bi_2O_3 are mixed for ten minutes in a mortar in different weight ratios;
- (iii) X-ray diffraction patterns of the mixture are obtained and the strongest peaks of both phases are simulated using Gauss functions, in order to calculate their intensity;
- (iv) the ratio between the number of bismuth atoms in the form of α - Bi_2O_3 ($n_{\text{Bi}_2\text{O}_3}$) and the number of bismuth atoms in the form of γ - $\text{Bi}_{12}\text{SiO}_{20}$ (n_{BSO}) is plotted versus the ratio between the intensities of the (120) $_{\text{Bi}_2\text{O}_3}$ and (310) $_{\text{BSO}}$ peaks. The curve presented in Fig. 2 is fitted using a three-degree polynomial.

4. Results

The evolution of the apparent density versus holding time, at 600°C , is presented in Fig. 3. The dedensification is continuous. The maximum volume expansion (56%) is observed after a 16 h holding time. Neither

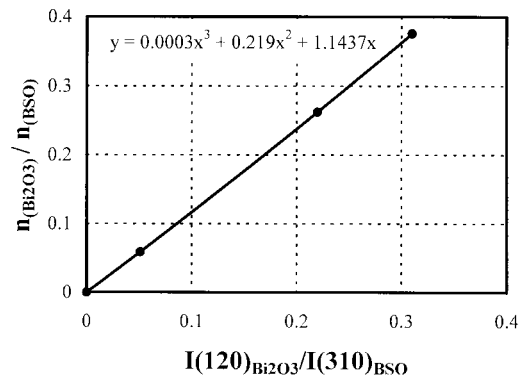


Fig. 2. Abacus used to determine the progress of BSO formation from the intensity of the characteristic X-ray diffraction peaks of BSO and α - Bi_2O_3 .

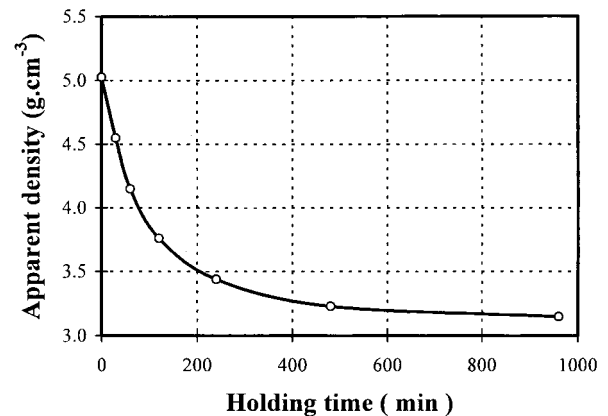
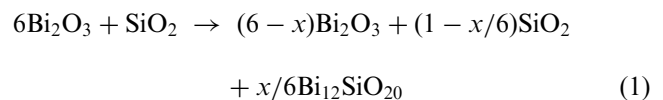


Fig. 3. Evolution of the sample relative density versus the holding time at 600°C .

further expansion, nor shrinkage, occurs afterwards at this temperature.

X-ray diffraction patterns of compacts heat-treated for 0, 60, 240 and 960 min at 600°C are presented in Fig. 4. α - Bi_2O_3 , γ - $\text{Bi}_{12}\text{SiO}_{20}$ and Bi_2SiO_5 are detected. The presence of this latter phase was already observed during the synthesis of γ - $\text{Bi}_{12}\text{SiO}_{20}$ powder at low temperature.⁶ Whatever the holding time, the amount of this minor phase is rather constant. The ratio between its strongest peak and the sum of $I_{\text{BSO}(310)}$ and $I_{\text{Bi}_2\text{O}_3(210)}$ is always less than 1%. Residual silica is never detected.

Neglecting the very small quantity of Bi_2SiO_5 , the progress of the synthesis reaction of γ - $\text{Bi}_{12}\text{SiO}_{20}$ can be expressed as x in the following equation:



where x represents the number of mol of reacted α - Bi_2O_3 in an initial mixture containing 6 mol of α - Bi_2O_3 and 1 mol of SiO_2 . For each holding time, x can be determined from the ratio between the intensities of the (120) $_{\text{Bi}_2\text{O}_3}$ and (310) $_{\text{BSO}}$ peaks, using the abacus presented

in Fig. 2. The evolution of x versus holding time at 600°C is shown in Fig. 5. The synthesis of BSO begins during the heating ramp but is most significant during the hold. After 16 h at 600°C, α -Bi₂O₃ is no longer detected, implying the reaction is complete.

5. Discussion

The results reported in Figs. 3 and 5 show that the volume expansion occurs during the formation of BSO. A variety of mechanisms can lead to large dedensification, but the following do not seem to be suitable candidates for the explanation of our results:

- (i)- formation and growth of strongly anisotropic grains of BSO. The grains formed during the reaction do not present any significant anisotropy (Fig. 6).
- (ii)-strong decrease of the average relative density of the constituent phases during the transformation

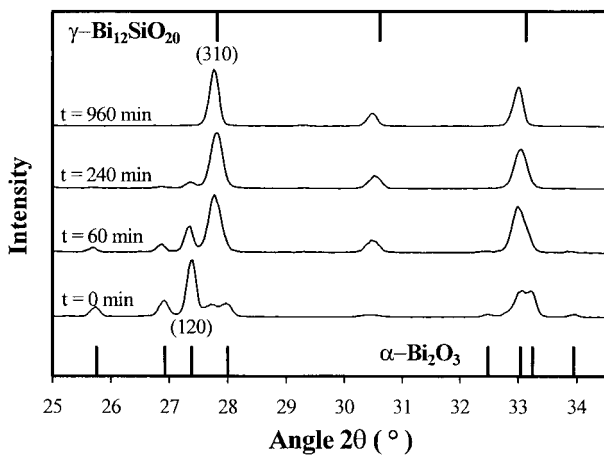


Fig. 4. X-ray diffraction pattern of the products obtained after different holding times at 600°C.

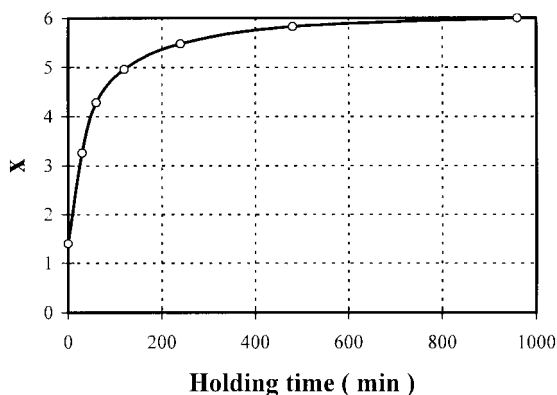
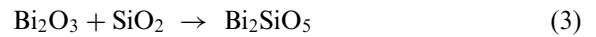


Fig. 5. Evolution of the number of reacted α -Bi₂O₃, x , versus holding time at 600°C.

from reactants to final products. Molar volumes of α -Bi₂O₃, SiO₂, α -Bi₁₂SiO₂₀ and Bi₂SiO₅ are, respectively, $V_{\text{Bi}_2\text{O}_3} = 49.78 \text{ cm}^3$, $V_{\text{SiO}_2} = 22.67 \text{ cm}^3$, $V_{\text{BSO}} = 310.76 \text{ cm}^3$ and $V_{\text{Bi}_2\text{SiO}_5} = 66.17 \text{ cm}^3$. This means that the relative matter volume variations corresponding to the completion of the reactions:



and



which are respectively -3.3 and -8.7% , cannot account for the observed expansion ($+56\%$).

- (iii)-trapping of gas in closed pores. When gas is released in a ceramic, volume expansion can occur if the pressure inside the closed pores increases strongly or if a liquid is present. Such a phenomenon is associated with a mass loss or, in the presence of a liquid, to the formation of very large and spherical pores. During heat-treatment, the observed mass loss is time independent and pores are not especially spherical in the resulting material. Therefore, a formation and escape of gas cannot account for the observed progressive volume expansion.

In the initial mixture, silica and bismuth oxide represent, respectively, 7 and 93% of the solid volume. Therefore, the microstructure of the sample, before reaction, can be considered as a dispersion of SiO₂ grains in a continuous matrix of α -Bi₂O₃ particles. In the early stage of the reaction, a BSO layer is formed at the surface of isolated SiO₂ particles. As discussed previously the volume of the BSO layer is less than the sum of the volumes of reacted silica and bismuth oxide. Therefore, the growth of isolated inclusions formed of a

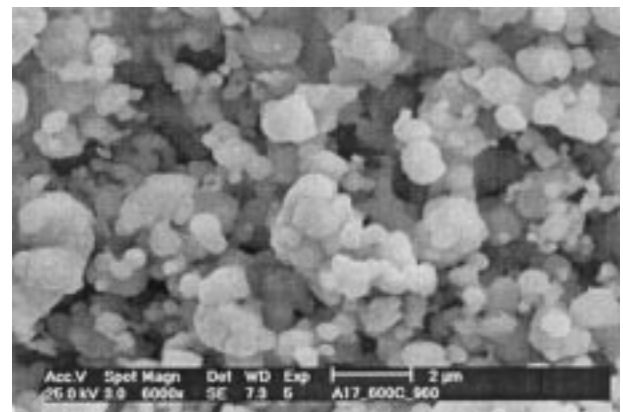


Fig. 6. Morphology of a sample treated at 600°C for 960 min.

SiO₂ grain surrounded by a BSO layer is not able to put the matrix under tensile stress and be the cause of an expansion of the sample volume.

When the amount of formed BSO is high enough to constitute a continuous skeleton in which the unreacted cores of the initial SiO₂ particles are dispersed, the behavior depends on the nature of the fastest matter transfer. If the reaction is controlled by a fast migration of Bi₂O₃, through the formed layer of BSO, towards SiO₂, the large difference between the molar volumes of SiO₂ and BSO must result in an expansion of the continuous BSO skeleton and consequently of the sample due to geometrical effect.^{8,9}

The variation of the apparent volume of a sample containing initially 6 mol of α-Bi₂O₃ and 1 mol of SiO₂ with the number, x , of reacted α-Bi₂O₃ presented in Fig. 7 is deduced from the results reported in Fig. 3 and 5. Three different domains can be distinguished:

- domain I ($x < 1.3$), the sample volume, V , is x independent;
- domain II ($1.3 < x < 5$), V increases progressively with x ;
- domain III ($x > 5$), V is a linear function of x .

The first domain (I) should correspond to the progressive growth of the isolated inclusions formed by a SiO₂ grain surrounded by a BSO layer. When BSO thick layers begin to be interconnected, the relation between the sample volume and x must be complex, due to interactions between the BSO and α-Bi₂O₃ continuous skeletons. The intermediate domain (II) could correspond to such a situation.

When the amount of formed BSO is high enough, the grains of unreacted α-Bi₂O₃ are isolated and the sample expansion must be directly related to the development of the BSO based continuous skeleton associated with the transformation of SiO₂. In absence of sintering phenomena, such an expansion can be considered as the

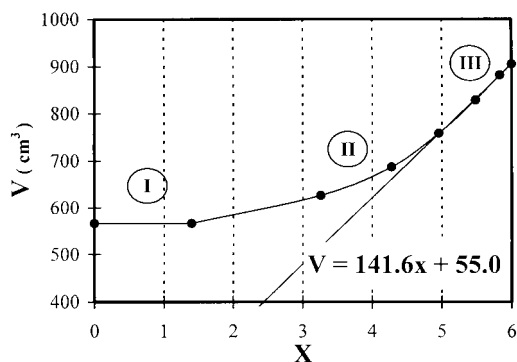


Fig. 7. Evolution of the apparent volume of a sample containing initially 6 mol of α-Bi₂O₃ and 1 mol of SiO₂ versus the number, x , of reacted α-Bi₂O₃.

result of isotropic growth of a constant number of BSO based grains.

Let us consider an initial cubic sample containing a mixture of 6 mol of α-Bi₂O₃ and 1 mol of SiO₂. When the expansion is controlled by the development of the BSO based skeleton, the sample volume, V_x , observed when the number of reacted α-Bi₂O₃ moles is x , is linked to the average radius, R_x , of the BSO based particles by the relation

$$V_x = (2NR_x)^3 \quad (4)$$

where N is constant and equal to the number of BSO based particles along a cube edge. $d(V_x)$ can be expressed by

$$d(V_x) = 24N^3(R_x)^2 d(R_x) \quad (5)$$

The volume, V_{p_x} , of a spherical BSO based particle is related to the molar volumes of BSO and SiO₂, respectively, V_{BSO} and V_{SiO_2} , by

$$V_{p_x} = (4/3)\pi(R_x)^3 = n(1 - x/6)V_{\text{SiO}_2} + n(x/6)V_{\text{BSO}} \quad (6)$$

where n is equal to the number of moles of Si in a BSO based particle and, then finally, to the moles number of BSO in a final grain. n is related to the radius R_6 of the final grains by the following relation:

$$n = 4\pi(R_6)^3 / (3V_{\text{BSO}}) \quad (7)$$

Deriving (6), gives

$$4\pi(R_x)^2 d(R_x) = (n/6)(V_{\text{BSO}} - V_{\text{SiO}_2}) dx \quad (8)$$

From Eqs. (5) and (8), it is possible to express $d(V_x)/dx$ as follows:

$$d(V_x)/dx = (V_{\text{BSO}} - V_{\text{SiO}_2})(nN^3)/\pi \quad (9)$$

N^3 can be deduced from the final volume of the sample, V_6 , using Eq. (4)

$$N^3 = V_6 / (8(R_6)^3) = M_{\text{BSO}} / (8\rho_6(R_6)^3) \quad (10)$$

where M_{BSO} and ρ_6 are, respectively, the mass of BSO and the apparent density of the final sample. Combining (7), (9) and (10), it gives finally

$$d(V_x)/dx = (V_{\text{BSO}} - V_{\text{SiO}_2})\rho_{\text{BSO}} / (6\rho_6) \quad (11)$$

where ρ_{BSO} (9.19 g cm⁻³) is the bulk density of BSO.

In the conditions of this study, the reaction is complete after 16 h at 600°C and the corresponding value of ρ_6 is 3.14 g cm⁻³. V_{SiO_2} and V_{BSO} being, respectively, 22.67 and 310.76 cm³, Eq. (11) leads to

$d(Vx)/dx = 140.4$. This calculated value is very close to the experimental slope, 141.6, observed for $x > 5$ (Fig. 7). A similar agreement is obtained for experiments performed with smaller α - Bi_2O_3 grains (specific surface area equal to $4.2 \text{ m}^2 \text{ g}^{-1}$). For a sample with an initial apparent density of 4.5 g cm^{-3} , the measured and calculated slopes are, respectively, 149.6 and 148.0.

A rapid matter transfer of SiO_2 , through a formed layer of γ - $\text{Bi}_{12}\text{SiO}_{20}$, towards α - Bi_2O_3 would also lead to a volume expansion. The maximum conceivable value calculated for a complete reaction, +4%, is too small to account for the experimental one (56%).

The sample volume variations observed during the reaction between α - Bi_2O_3 and SiO_2 are the same as those which would be observed, in absence of sintering, if the matter transfer is controlled by diffusion of α - Bi_2O_3 , through the layer of γ - $\text{Bi}_{12}\text{SiO}_{20}$, towards SiO_2 .

6. Conclusion

The synthesis of γ - $\text{Bi}_{12}\text{SiO}_{20}$ from a compact mixture of α - Bi_2O_3 and SiO_2 leads to a very large volume expansion, which can reach 56%. This dedensification can be considered as the result of a reaction controlled by the diffusion of bismuth and oxygen ions towards SiO_2 , through the layer of γ - $\text{Bi}_{12}\text{SiO}_{20}$ formed around silica grains. It begins when the γ - $\text{Bi}_{12}\text{SiO}_{20}$ phase constitutes a continuous skeleton. When bismuth oxide grains are isolated in the γ - $\text{Bi}_{12}\text{SiO}_{20}$ skeleton, the volume change and the reaction rates are proportional each other.

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References

1. Aldrich, R. E., Lou, S. L. and Harvill, M. L., Electrical and optical properties of $\text{Bi}_{12}\text{SiO}_{20}$. *J. Appl. Phys.*, 1971, **42**, 493–494.
2. Abrahams, S. C., Bernstein, J. L. and Svensson, C., Crystal structure and absolute piezoelectric d_{14} coefficient in laevorotatory $\text{Bi}_{12}\text{SiO}_{20}$. *J. Chem. Phys.*, 1979, **71**, 789–792.
3. Ballman, A., The growth and properties of piezoelectric bismuth germanium oxides $\text{Bi}_{12}\text{GeO}_{20}$. *J. Crystal Growth*, 1967, **1**, 37–40.
4. Nomura, K. and Ogawa, H., $\text{Bi}_{12}\text{SiO}_{20}$ thin films grown by electron cyclotron resonance plasma sputtering with Bi and Si multitarget system. *Jpn. J. Appl. Phys.*, 1991, **30**, 3796–3801.
5. Mitsuyu, T., Wasa, K. and Hayakama, S., Structures and optical properties of RF-sputtered $\text{Bi}_{12}\text{GeO}_{20}$ films. *J. Electrochemical Soc.*, 1976, **123**, 94–96.
6. Fu, Senlin and Ozoe, H., Reactions pathways in the synthesis of photorefractive γ - $\text{Bi}_{12}\text{MO}_{20}$, M = Si, Ge, Ti. *J. Am. Ceram. Soc.*, 1997, **80**, 2501–2509.
7. Morell, A. and Hermosin, A., Sintering of an X-ray photosensitive ceramic: $\text{Bi}_{12}\text{SiO}_{20}$. *J. Am. Ceram. Soc.*, 1979, **58**, 613–615.
8. Anseau, M. R., Cambier, F. and Leblud, C., Some comments on ceramic solid-state reaction kinetics using results obtained on the $\text{ZnO-Al}_2\text{O}_3$ system. *J. Mater. Sci.*, 1981, **16**, 121–1126.
9. Cambier, F., Leblud, C. and Anseau, M. R., Reaction sintering of MgO-TiO_2 mixtures. *Ceram. Intern.*, 1982, **8**, 77–78.