Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Crystal structure and thermal behavior of a new borosilicate with the CAS framework type

Maria G. Krzhizhanovskaya [a,*], Rimma S. Bubnova [b], Wulf Depmeier [c], Stanislav K. Filatov [a], Valeriy L. Ugolkov [b]

[a] Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034, St. Petersburg, Russian Federation
[b] Institute of Silicate Chemistry of RAS, Makarova Emb. 2, 199034, St. Petersburg, Russian Federation
[c] Institut für Geowissenschaften, University of Kiel, Olshausenstrasse 40, D-24118, Kiel, Germany

ARTICLE INFO

ABSTRACT

The crystal structure of the new microporous framework borosilicate $|Cs_4||B_4Si_{20}O_{48}|$-CAS has been studied using X-ray diffraction data on powders prepared by solid state reaction as well as by glass crystallization. It is isostructural with $|Cs_4||Al_4Si_{20}O_{48}|$-CAS and belongs to the zeolite framework type CAS. Non-random distribution of the Si and B atoms over the tetrahedral positions has been revealed.
The behavior of $|Cs_4||B_4Si_{20}O_{48}|$-CAS on heating was studied using high-temperature X-ray diffraction HTXRD, differential thermal analysis (DTA) and annealing series. According to HTXRD data the thermal deformation of $|Cs_4||B_4Si_{20}O_{48}|$-CAS has anisotropic character with the maximum expansion along the infinite channels, where the Cs atoms are located.
The DTA and heat treatment studies showed that during the solid state reaction the first phase to crystallize at about 800 °C is the boropollucite $CsBSi_2O_6$, which beyond 900 °C transforms into $|Cs_4||B_4Si_{20}O_{48}|$. Around 1100 °C a final decomposition occurs according to the reaction $|Cs_4||B_4Si_{20}O_{48}| \rightarrow 20SiO_2 + 4CsBO_2\uparrow$.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

Until recently the crystal chemistry of alkali borosilicates, the main source of the technologically important borosilicate glasses [1], is studied poorly in comparison with the corresponding aluminosilicates. For many years attempts to synthesize stable compounds via solid state reactions or glass crystallization methods in the ternary borosilicate systems $R_2O–B_2O_3–SiO_2$ (R = K, Rb, and Cs) were successful for only one stoichiometry, viz. $R_2O \times B_2O_3 \times 4SiO_2$ (R = K [2,3], Rb [4–6], and Cs [7,8]. All these compounds have a tetrahedral framework structure corresponding to that of the analcime-leucite family (ANA) of aluminosilicates. In addition to the leucite-like compounds $|R_{16}||B_{16}Si_{32}O_{96}|$-ANA (R = K, Rb, and Cs) in the ternary $R_2O–B_2O_3–SiO_2$ (R = K, Rb, and Cs) systems, structural data have been reported for hydrothermally prepared $KBSi_3O_8$ [9], which is isostructural with danburite, $CaB_2Si_2O_8$, and lisitzynite, $KBSi_2O_6$, reported in [10] as a boroleucite polymorph. Additionally, there are XRD data for some low temperature potassium borosilicates [11] and Refs. therein and a presumably metastable low temperature polymorph of $|Cs_{16}||B_{16}Si_{32}O_{96}|$-ANA [12]. The structures of all these compounds have not been solved yet.

Recently, a borosilicate of another stoichiometry, $CsBSi_5O_{12}$ ($\equiv|Cs_4||B_4Si_{20}O_{48}|$-CAS), has been prepared from the initial boropollucite $CsBSi_2O_6$ (ANA) by long-term high-temperature annealing at temperatures beyond 1000 °C. The mechanism of the $CsBSi_5O_{12}$ formation via the boropollucite decomposition has been studied in our previous work using annealing, DSC (differential scanning calorimetry) and TG (thermogravimetry) methods [13]. From powder XRD data the new borosilicate was proposed to be isostructural with $|Cs_4||Al_4Si_{20}O_{48}|$, the latter having a zeolite framework of type CAS [14]. Based on single crystal work [15], the Si and Al atoms in the aluminosilicate framework of $|Cs_4|$-$[Al_4Si_{20}O_{48}]$ were reported to be randomly distributed over three tetrahedral positions. Later high-resolution powder neutron diffraction [16] led the authors to propose an ordered distribution with Al having a certain preference for one of the tetrahedra. The most recent study on $|Cs_4||Al_4Si_{20}O_{48}|$-CAS [17] did not confirm the ordered distribution of the tetrahedral cations in the structure.

Our present paper reports on the crystal structure of the new $|Cs_4||B_4Si_{20}O_{48}|$-CAS borosilicate from powder X-ray diffraction data. Its thermal behavior is studied using both, HTXRD and DTA methods.

2. Experimental

2.1. Preparation

Polycrystalline $|Cs_4||B_4Si_{20}O_{48}|$-CAS was first synthesized by standard solid state techniques (sample I in Table 1), viz. from

* Corresponding author.
  E-mail address: krzhizhanovskaya@mail.ru (M.G. Krzhizhanovskaya).

Table 1
Crystallographic data for $|Cs_4|[B_4Si_{20}O_{48}]$-CAS

Sample number	I	II
Composition of initial mixture	8.3/8.3/83.4	12.5/12.5/75
Cs_2O / B_2O_3 / SiO_2 (mol%)		
Method of preparation	Solid state reaction	Glass crystallization
T (°C)/exposition	1000/11 h +1070/5 h	1090/14 h
Space group, Z	Ama2, 4	Ama2, 4
a (Å)	16.2312(5)	16.2244(5)
b (Å)	13.3655(4)	13.3617(4)
c (Å)	4.8733(1)	4.8755(1)
V (Å³)	1057.19(5)	1056.93(5)
2θ – range (degrees)	16–96	16–96
R_p	5.73	6.06
R_{wP}	7.89	7.98
R_{exp}	3.32	4.32
χ^2	5.64	3.40
R_B	6.79	5.97
R_F	5.38	4.12
Weight% $|Cs_4|[B_4Si_{20}O_{48}]$	62.6	87.2
Weight% SiO_2 (cristobalite)	37.4	12.8

H_3BO_3, Cs_2CO_3 and hydrated SiO_2 reagents mixed in appropriate proportions with mass losses due to dehydration taken into account. In accordance with reports on $|Cs_4|[Al_4Si_{20}O_{48}]$-CAS [18], the initial weight of Cs_2CO_3 was reduced by two weight% with a view to avoid formation of a boropollucite (ANA) phase. The Cs carbonate was calcined at 500 °C for 3 h. In a first run, compressed tablets of the thoroughly mixed educts were put in a platinum crucible and annealed at 1000 °C for 11 h in air. Despite the reduced amount of calcined Cs_2CO_3 we were not able to avoid the formation of boropollucite as an intermediate product. Only after a further treatment at 1070 °C for 5 h no more pollucite could be detected, however the sample contained a great amount (about 40%) of cristobalite.

With the aim to prepare cristobalite-free samples we used borosilicate glass obtained at 1300 °C for 1 h from a mixture of 12.5 mol% Cs_2O, 12.5 mol% B_2O_3 and 75 mol% SiO_2 (sample II in Table 1) corresponding to the stoichiometry $CsBSi_3O_8$. The glass powder was heat treated at 1090 °C for 14 h. In spite of the composition considerably shifted from the SiO_2 corner of the system the product still contained a considerable amount (about 15 weight%) of cristobalite.

2.2. Structure refinement

The diffraction data for Rietveld analysis were collected in air at room temperature on a D5000 diffractometer (Bruker, 40 kV/30 mA, CuKα λ = 1.5418 Å radiation, graphite monochromator, and scintillation detector) for both synthesized samples in the 2θ range 10°–100°. The step scan mode with step width 0.02 in 2θ and 10 s general exposition per point was used. The structure refinement was carried out with the program Fullprof [19]. Scattering factors for neutral atoms were used. The background was modeled using a 7th order polynomial approximation. The peak-profiles were described by a Pseudo-Voigt function. The refinement of asymmetry and preferred orientation (March-Dollase function) parameters did not suggest any considerable asymmetry or preferred orientation in the studied samples.

2.3. High-temperature X-ray and DTA study

The thermal behaviour of the new CAS borosilicate upon heating in air was studied by high-temperature X-ray powder diffractometry employing a DRON 3 M diffractometer (NPO Burevestnik; 35 kV/20 mA; CuKα λ = 1.5418 Å radiation, graphite monochromator and scintillation detector) in the 20–700 °C tem-

perature range. The cell parameters at different temperatures were calculated using standard least-squares methods with the UnitCell program [20]. Silicon was used as external standard. Temperature dependencies of unit cell parameters were described by linear (a and c parameters) and quadratic (b and V) approximations.

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed on a Netzsch derivatograph for the initial charge of H_3BO_3, Cs_2CO_3 and hydrated SiO_2 heated at 800 °C for 3 h and for the sample I (see Table 1). The heating rate was about 10 K/min. Approximately 30 mg of powder sample placed in a platinum crucible was used.

3. Results and discussions

3.1. Structure refinement

Differences between the lattice parameters of samples I and II do not exceed 0.05% of the absolute parameter values $(a(I)-a(II) = 0.042\%$, $b(I)-b(II) = 0.028\%$, $c(I)-c(II) = 0.045\%$, see Table 1).

A Rietveld refinement has been performed for both synthesized samples. The atomic positions of $|Cs_4|[Al_4Si_{20}O_{48}]$ [15] and statistical distribution of boron and silicon atoms over three non-equivalent tetrahedral sites in space group A$ma2$ were taken as a starting model, including individual isotropic atomic displacement parameters (adp). From the refinement it became clear that a model with ideal statistical distribution of the T atoms (T = Si and B) does not fit the diffraction data in our case of $|Cs_4|[B_4Si_{20}O_{48}]$. The refined adp of the tetrahedral cations were obviously unreliable, with the values of T3 being positive, while those of T1 and T2 were strongly negative. In addition, the interatomic T–O distances clearly did not fit into the parameter range normally found for borosilicates with a 5:1 ratio of Si–B. In contrast, the adp of the oxygen atoms were normal as well as the O–O distances with values around 2.5 Å, typical for borosilicate tetrahedra. Obviously, the problem pertained to the distribution pattern of the central tetrahedral atoms. Several models for the Si–B distribution were tested. In one of them both, boron and silicon, shared the same tetrahedral positions, but with slightly different proportions. This model satisfied most of our experimental data and is considered as correct. The refinement results are presented in Table 1. Virtually the same results were obtained for refinements with data from both differently prepared samples. We consider this fact as a further confirmation of the correctness of our model. The observed, calculated and difference curves for the experiments are shown in Fig. 1a and b for samples I and II, respectively. The final atomic parameters are presented in Table 2a and b for samples I and II, respectively. A similar situation with random or non-random T atom distribution was described in [16], where the authors tried different models for the isostructural $|Cs_4|[Al_4Si_{20}O_{48}]$ and finally concluded that the distribution of silicon and aluminium was not random, but that aluminium exhibited a preference for one of the three tetrahedral sites. The model of [16] was also tested by us but their refined parameters did not satisfy our experimental data as well as the one shown in Table 2.

Since the lattice parameters as well as the atomic coordinates of both samples are virtually the same (Tables 1, 2a and b), we restrict ourselves to a discussion of the results of the refinement performed on the sample II, because of its lower content of accessory SiO_2. The substantial deficiency on the cesium position (Table 2) is probably caused by the loss of Cs during the heat treatment beyond 1000 °C. In order to keep the electron neutrality of the structure the Si–B ratio was decreased appropriately. It should be noted that according to wet chemistry data substantial mass losses in Cs and B occurred for $|Cs_{16}|[B_{16}Si_{32}O_{96}]$-ANA boropollucite samples when