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Thermal expansion behavior in the solid solution series $BaMg_{2-x}Co_xSi_2O_7$ ($0 \leq x \leq 2$), studied by dilatometry and in situ high-temperature X-ray diffraction

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ABSTRACT

In the compound $BaMg_2Si_2O_7$, the Mg^{2+}-ions can completely be replaced by Co^{2+}-ions. The resulting solid solutions show a phase transition from a low to a high temperature phase. Both, the thermal expansion behavior as well as the phase transition temperature change significantly with the Mg/Co-ratio. The phase transition runs parallel to an increase in volume, which can be detected using dilatometry. The introduction of small CoO concentrations leads to an increase in the phase transition temperature. In order to determine the thermal expansion behavior, dilatometry, as well as high temperature X-ray diffraction was used. The substitution of MgO by up to 50 mol% CoO does not lead to a significant change in the thermal expansion behavior. The measured coefficients of thermal expansion lie in a range between 7.0 and $24.0 \times 10^{-6}\,K^{-1}$.

1. Introduction

Crystallizing glasses with high coefficients of thermal expansion, based on the systems $BaO–MO–SiO_2$, with MO = CaO, MgO or ZnO are well known as suitable candidates for sealing materials in high temperature reactors, such as the solid oxide fuel cell (SOFC) [1,2]. In these reactors, hermetic and electrical insulating seals are required in order to join different ceramic and metallic components [3]. One of the main reasons causing a failure of such a joint is the thermal expansion mismatch between the different parts [4]. Hence, thermal induced stresses at the interface, resulting from thermal cycling between room temperature and the operation temperature of an SOFC (700–900 °C), should be minimized by tuning the thermal expansion behavior of the glass ceramic seal [5]. The coefficients of thermal expansion (CTE) of the seal and the materials, contacted to the seal should be approximately the same. Furthermore, the CTEs of the crystalline phases should be constant in the entire temperature range between room temperature and the operating temperature of the high temperature reactor [6] or, however, should change in the same manner in all decisive components. In SOFCs high temperature resistant alloys such as nickel base alloys or certain stainless steels are used as the metallic component [7,8]. All alloys proposed for SOFCs have CTEs $>10 \times 10^{-6\,K-1}$. Nickel alloys even exhibit values of up to $19 \times 10^{-6}\,K^{-1}$ [9]. The CTEs of the various ceramic materials, which can be applied as anodes or cathodes for high temperature reactors are somewhat smaller than the CTEs of Ni-alloys, but have also a value higher than $10 \times 10^{-6}\,K^{-1}$ [10]. According to the applied materials, the CTE of the glass ceramic sealing material has to match with the components, contacted to the seal. Hence, also the CTEs of the crystal phases, which mainly affect the thermal expansion behavior of the glass–ceramic seal should exhibit CTEs larger than $10 \times 10^{-6}\,K^{-1}$. Some binary and ternary BaO containing silicates exhibit such high CTEs [11,12].

The thermal expansion of silicates containing BaO, ZnO and CaO has already been studied using dilatometry and high temperature X-ray diffraction (HT-XRD) [11–13]. The determination of the thermal expansion behavior by dilatometry is a simple method, where phase transitions, which run parallel to a volume change, can easily be detected [14]. However, the CTE is strongly affected by the preparation method (e.g. isostatical pressing, uniaxial pressing, sintering etc.) and the conditions supplied. Nevertheless, dilatometry is a good tool for estimating the thermal expansion behavior as suitable for the application in SOFCs.

HT-XRD, in comparison to dilatometry, is a more time-consuming method. Nevertheless, using this technique each lattice parameter and the volume of the unit cell can be determined as a function of temperature [12]. However, phase transitions, running parallel to an abrupt change in the cell volume, are easy to detect

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by dilatometry, while they might be difficult to identify using HT-XRD if the changes in the XRD-patterns during phase transition are only small [14]. If such transitions cause significant structural changes, the patterns can be evaluated using Rietveld refinement [15].

Commonly, sealing materials for the application in high temperature reactors are used in form of glass powders, brought in between the components to be joint [1]. At first, the powder is sintered in the glassy state as a result of viscous flow until nearly complete densification is achieved. This stage is reached by a temperature treatment at the respective temperature. During this step the seal is joined to the other materials. In a subsequent second step, the glass crystallizes at the respective crystallization temperature and the final glass ceramic is formed.

The crystallization process often leads to the formation of oriented crystals, i.e. certain crystallographic directions have a preferred orientation [16–18]. This has already been reported, especially from glasses, showing surface crystallization [19–22]. So it is highly possible that there are oriented structures at the interface between the glass ceramics and the adherent materials in an SOFC. Some crystal phases, such as $BaZnSiO_4$ or $BaSi_2O_5$ exhibit CTEs, extremely depending on the lattice parameters [12,13]. For example, the CTEs in different crystallographic directions of the unit cell of $BaZnSiO_4$ vary between 7.0 and $15.1 \times 10^{-6}\,K^{-1}$ and the CTEs of $BaSi_2O_5$ vary between 10.6 and $21.7 \times 10^{-6}\,K^{-1}$ [12,13]. Hence, an unfavorable and non-statistical orientation of crystals at the interface between the joint materials can lead to a thermal expansion behavior, fairly different from that of the bulk material, causing a destruction of the interface during thermal cycling.

In the system $BaO–MgO–SiO_2$ data on the thermal expansion behavior of crystal phases have not yet been reported in the literature. Besides this system, glasses containing BaO, CoO and SiO_2 as the main constituents were also investigated as possible candidates for sealing materials with very good adhesion properties [23]. The ternary silicates $BaMg_2Si_2O_7$ and $BaCo_2Si_2O_7$ were already investigated by dilatometry and HT-XRD and showed a favorably high thermal expansion behavior [14,24]. According to the ICSD database, these phases are isostructural and crystallize in a monoclinic crystal lattice with the space group C12/c1 (see Refs. [25,26] or ICSD 420258 and 81473). $BaCo_2Si_2O_7$ and $BaMg_2Si_2O_7$ show phase transitions from low into high temperature modifications at temperatures of 850 and 937 °C, respectively [13,14]. The crystal structure of the high temperature modification could not be refined in Ref. [14], but it can be assumed that the crystal structure is similar to that of orthorhombic high temperature $BaZn_2Si_2O_7$, already reported in the literature [15]. The monoclinic phase $BaCo_2Si_2O_7$ shows a more isotropic thermal expansion with the lowest CTE in the direction of the lattice parameter *c* with a value of $9.6 \times 10^{-6}\,K^{-1}$ [14]. The highest CTE is that of the lattice parameter *b*, which is $14.8 \times 10^{-6}\,K^{-1}$ [14]. $BaMg_2Si_2O_7$ exhibits an even stronger anisotropic behavior with CTEs between 6.2 and $19.9 \times 10^{-6}\,K^{-1}$, depending on the respective crystallographic direction. Commonly, sealing materials in SOFCs are contacted to other materials, containing numerous different elements so that solid solutions can be formed during the operation of the cell. Amongst others, such elements often can be Co and Ni in lanthanum cobaltate or nickel/YSZ cermets [27]. In this publication the thermal expansion behavior in the solid solution series $BaMg_{2-x}Co_xSi_2O_7$ ($0 \le x \le 2$) was analyzed using dilatometry and HT-XRD.

2. Experimental

Ternary silicates from the solid solution series $BaMg_{2-x}Co_xSi_2O_7$ ($0 \le x \le 2$) were synthesized via conventional ceramic route. Mixtures of SiO_2 (Carl Roth GmbH + Co. KG, >99%), $BaCO_3$ (VK Labor- und Feinchemikalien, pure), Co_3O_4 (VEB Laborchemie Apolda, pure) and MgO (Merck KGaA, heavy extra pure) were used as raw materials. The mixtures were heated up to temperatures between 1125 and 1250 °C, kept for 30–50 h with several intermediate regrinding steps. The phase purity was verified by X-ray powder diffraction (XRD), using a SIEMENS D5000 diffractometer and Cu Kα radiation. The XRD-patterns of the powdered samples were recorded between $10 \le 2\theta \le 60°$ with a step size of $\Delta\theta = 0.02°$ and a counting time of 2–3 s per step. From these patterns, the cell parameters were calculated with the software MAUD (materials analysis using diffraction) [28]. The refinement of lattice parameters was done using whole powder pattern decomposition (Pawley method), as described in a previous publication [14]. The respective data sets from the ICSD data base were taken as the starting values of the refinement. Since the XRD patterns exhibit low intensities and relatively high background noise, a refinement of atom positions was not reasonable.

The high-temperature XRD (HT-XRD) measurements were performed, using a SIEMENS D5000 Bragg–Brentano diffractometer with an ANTON PAAR HTK 10 heating stage. The powdered samples were heated to the respective temperatures, kept for several minutes until temperature equilibrium is reached and afterwards an XRD scan was performed. The samples were measured in a 2θ range from 17 to 36°. This interval was adapted to the respective samples, so that the main diffraction peaks, necessary for a reproducible determination of lattice parameters, lie in it. All the samples, analyzed by HT-XRD contain 33wt% of α-Al_2O_3 as an internal standard. This is necessary for the correction of the sample displacement, caused by the thermal expansion of the sample holder at high temperatures. The peak positions and cell parameters of α-Al_2O_3 are known from the ICSD database (27 °C: ICSD10425, 300 °C: ICSD160605, 600 °C: ICSD160606, 900 °C: ICSD160607) as well as from the literature [29,30].

Dilatometric measurements were performed between room temperature and 1000 °C (heating rate 5 K/min), using a dilatometer NETZSCH Dil 402 PC. The ceramic powders were cold isostatically pressed into cylindrical shape (diameter: 6–8 mm, length: 5–25 mm) and afterwards sintered between 1125 and 1250 °C, kept for 10 h. From these dilatometric measurements, the phase transition temperatures were estimated, using the tangent method. The maximum error of the onset of the phase transition is ±10 K, including the temperature measuring error and the error of the tangent method.

3. Results and discussion

The dilatometric thermal expansion behavior in the solid solution series $BaMg_{2-x}Co_xSi_2O_7$ ($0 \le x \le 2$) is illustrated in Fig. 1. The temperatures attributed to the transition of the low to the high

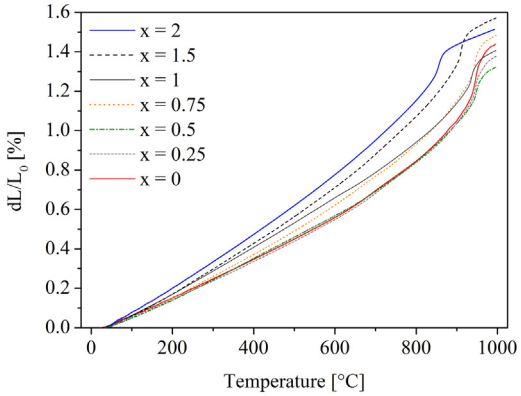

Fig. 1. Dilatometric measurements of the solid solution series $BaMg_{2-x}Co_xSi_2O_7$ ($0 \le x \le 2$).