

Negative Thermal Expansion in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_2\text{SiGeO}_7$

Christian Thieme * and Christian Rüssel

Otto-Schott-Institut für Materialforschung, Jena University, Fraunhoferstr. 6, Jena 07743, Germany; ccr@uni-jena.de

* Correspondence: christian.thieme@uni-jena.de; Tel.: +49-3641-948-525

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Abstract: Solid solutions with the composition $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ and $\text{BaZn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ were prepared with different values of x using a conventional mixed oxide route. Both compounds exhibit very different thermal expansion, which is due to the different crystal structures. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ solid solutions exhibit the structure of high-temperature $\text{BaZn}_2\text{Si}_2\text{O}_7$ and show negative thermal expansion, which was proven via high-temperature X-ray diffraction. Up to around $x = 1$, the crystal structure remains the same. Above this value, the low-temperature phase becomes stable. The Sr-free solid solutions have the crystal structure of low-temperature $\text{BaZn}_2\text{Si}_2\text{O}_7$ and show also a limited solubility of Ge. These Sr-free compositions show transitions of low- to high-temperature phases, which are shifted to higher temperatures with increasing Ge-concentration.

Keywords: X-ray diffraction; negative thermal expansion; phase transition

1. Introduction

The phase $\text{BaZn}_2\text{Si}_2\text{O}_7$ exhibits a phase transition at around 280 °C [1]. This phase transition divides the thermal expansion behavior into two parts. Below the phase transition, the monoclinic low-temperature phase (LT-phase) is stable, which has a very high coefficient of thermal expansion (CTE) [2]. Above the phase transition, the orthorhombic high-temperature phase (HT-phase) is stabilized with its very low or even negative thermal expansion behavior [2]. The crystal structures of both phases are described in the literature. The LT-phase has the space group $C2/c$ [1]. The space group of the HT-phase is $Ccm2_1$ and is also reported in reference [1], where in-situ measurements were performed at high temperatures. However, the crystal structure was also refined in reference [3] using single crystals from a solid solution and a slightly different but very similar result (space group $Cmcm$) was obtained. However, the lattice parameters are defined differently in [1,3], which can easily lead to confusions. Hence, this work is based on the crystal structure reported in reference [3].

The $\text{BaZn}_2\text{Si}_2\text{O}_7$ phase forms solid solutions within wide concentration ranges leading to a shift of the phase transition temperature depending on the site, which is occupied by other ions with the same valence state and similar ionic radii. A replacement of the Zn^{2+} -ions by Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} leads to a shift of the phase transition to higher temperatures, this is, a stabilization of the LT-phase in a wider temperature range [4]. If the Ba^{2+} -ions are replaced by Sr^{2+} , the phase transition temperature decreases and if a certain concentration of Sr^{2+} is exceeded, the HT-phase with its low thermal expansion is stable even below room temperature [3,4].

Materials containing high concentrations of alkaline earth oxides normally exhibit very high CTEs and a low thermal expansion might be unexpected or even undesired as in the case of sealing glasses or glass-ceramics for HT-reactors [5–7]. Hence, a detailed knowledge on the phase transition temperature for both the HT- as well as the LT-phase is necessary in order to control the thermal expansion behavior of materials, especially of glass-ceramics being able to precipitate the described solid solutions [8].

Furthermore, the crystalline solid solutions mentioned above exhibit CTE values, which strongly depend on the crystallographic direction and the composition. Especially in the case of phases with the

structure of HT-BaZn₂Si₂O₇, the CTEs of the different lattice parameters vary strongly [4,9]. The reason for this behavior is described in reference [3] to be caused by the crystal structure, which is composed of ZnO₄ chains, running through the crystal in the direction of the lattice parameter *c*. These chains are connected by Si₂O₇ units. An increase of the temperature leads to a rotational movement of the ZnO₄ tetrahedra and hence, the chains are stretched, which causes very high thermal expansion in the direction of the crystallographic *c*-axis. In the direction of the *b*-parameter, the ZnO₄ tetrahedra are compressed, which causes highly negative thermal expansion.

This study reports on the influence of Ge⁴⁺ on the phase stability in Ba_{0.5}Sr_{0.5}Zn₂Si_{2-x}Ge_xO₇ and BaZnSi_{2-x}Ge_xO₇ solid solutions prepared via solid-state reaction. Furthermore, the thermal expansion of the compound Ba_{0.5}Sr_{0.5}Zn₂SiGeO₇ in the different crystallographic directions was checked with high-temperature X-ray diffraction (HT-XRD).

2. Results and Discussion

Figure 1 shows solid solutions of the form Ba_{0.5}Sr_{0.5}Zn₂Si_{2-x}Ge_xO₇ with different values of *x*. It can clearly be seen that samples with small Ge-concentrations exhibit the crystal structure of HT-BaZn₂Si₂O₇ (see left part of Figure 1). The substitution of Si by Ge also leads to a shift of the peaks in the direction of smaller 2θ-values, i.e., larger lattice parameters, which is due to the larger ionic radius of Ge⁴⁺ in comparison to Si⁴⁺ [10]. The increasing lattice parameters are displayed at the right side of Figure 1 as a function of *x* together with the respective linear regression. The composition Ba_{0.5}Sr_{0.5}Zn₂SiGeO₇ still exhibits the crystal structure of HT-BaZn₂Si₂O₇ without any impurity phases. At higher Ge-concentrations, the crystal structure of LT-BaZn₂Si₂O₇ becomes stabilized together with some secondary phases, which cannot reliably be identified.

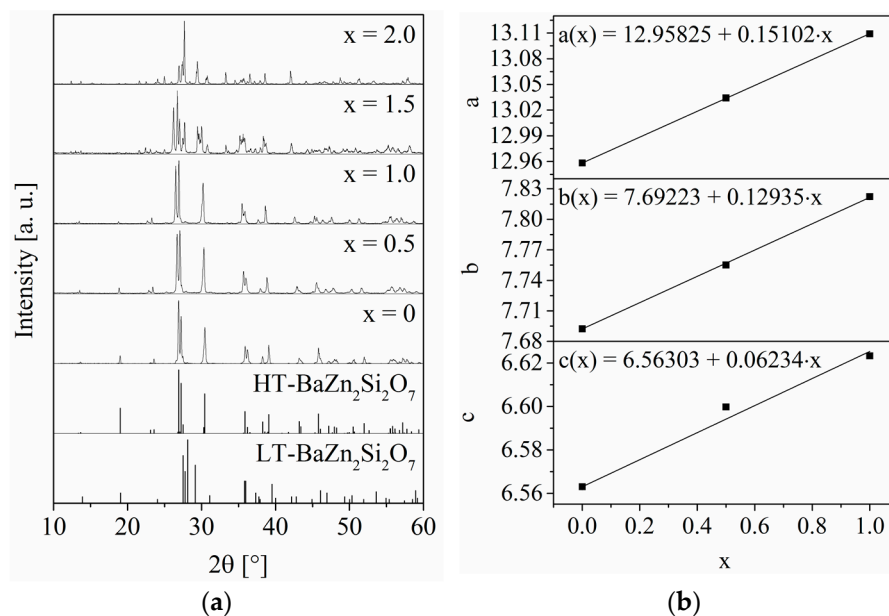


Figure 1. Results from X-ray diffraction (XRD) recorded at room temperature. (a) XRD patterns within the solid solution series Ba_{0.5}Sr_{0.5}Zn₂Si_{2-x}Ge_xO₇ with different values of *x* are shown. In the lower part, the theoretical peak positions of crystals with the structure of high-temperature (HT)- and low-temperature (LT)-BaZn₂Si₂O₇ taken from references [3,11] are displayed; (b) the lattice parameters of Ba_{0.5}Sr_{0.5}Zn₂Si_{2-x}Ge_xO₇ are shown as a function of *x*. The values for *x* = 0 were taken from reference [9].

A similar behavior was found in the case of the solid solution without Sr. By contrast, these compositions exhibit the crystal structure of LT-BaZn₂Si₂O₇ (diffractograms not illustrated here). The compound BaZn₂SiGeO₇ shows solely lines, which can be attributed to crystals with the structure

of LT-BaZn₂Si₂O₇. The compound BaZn₂Si_{0.5}Ge_{1.5}O₇ as well as the pure Ge-compound also show the crystal structure of LT-BaZn₂Si₂O₇, but also some minor phases appear, which is in agreement with the findings reported in reference [12].

The compound Ba_{0.5}Sr_{0.5}Zn₂SiGeO₇ was chosen in order to measure the thermal expansion behavior with HT-XRD. The lattice parameters of this composition can be fitted by second order polynomials. The corresponding regression parameters are summarized in Table 1. The relative change of the length of the lattice parameters a, b, and c as well as the volume of the unit cell V can be seen in Figure 2. As recently reported for the compound Sr_{0.5}Ba_{0.5}Zn₂Si₂O₇ with this crystal structure, the lattice parameter b contracts strongly upon warming, whereas the a and the c parameters show an increasing length. The overall volume of the unit cell decreases with increasing temperature up to around 400 °C–500 °C. At higher temperatures, the volume of the unit cell increases. Between 600 and 1000 °C, this increase is almost linear.

Table 1. Regression parameters describing the temperature dependence of the lattice parameters a, b, and c of the compound Ba_{0.5}Sr_{0.5}Zn₂SiGeO₇ using a polynomial of the form: $y(T) = A + BT + CT^2$.

Regression Parameters		a	b	c
A (Å)	value	13.10577	7.83397	6.61951
	std. error.	0.00266	0.00435	9.32275×10^{-4}
B (Å/°C)	value	1.87277×10^{-4}	-4.29385×10^{-4}	1.77221×10^{-4}
	std. error.	1.23447×10^{-5}	2.0211×10^{-5}	4.32873×10^{-6}
C (Å/°C ²)	value	-6.65004×10^{-8}	2.19955×10^{-7}	-2.78727×10^{-8}
	std. error.	1.17341×10^{-8}	1.92113×10^{-8}	4.11461×10^{-9}

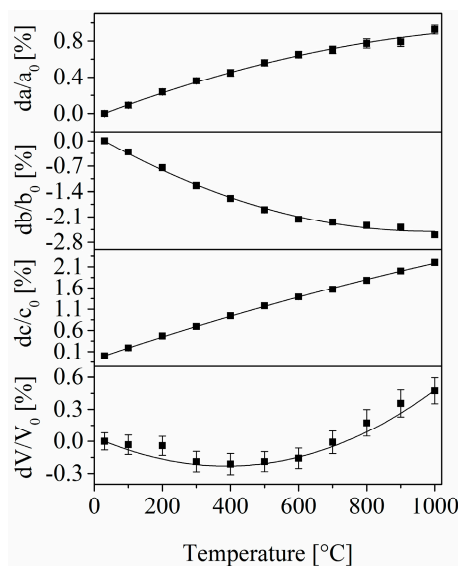


Figure 2. Relative change of the lattice parameters of Ba_{0.5}Sr_{0.5}Zn₂SiGeO₇ determined with HT-XRD. The values a_0 , b_0 , c_0 , and V_0 were determined at room temperature. The line, which fits the change of the volume of the unit cell was calculated on the basis of the regression parameters given in Table 1.

The compound is highly anisotropic with CTEs of $13.4 \times 10^{-6} \text{ K}^{-1}$ (lattice parameter a), $-45.7 \times 10^{-6} \text{ K}^{-1}$ (lattice parameter b), and $25.7 \times 10^{-6} \text{ K}^{-1}$ (lattice parameter c) measured between 30 and 300 °C. Between 30 and 800 °C, the anisotropy is a little bit smaller with CTEs of $10.1 \times 10^{-6} \text{ K}^{-1}$ (lattice parameter a), $-30.4 \times 10^{-6} \text{ K}^{-1}$ (lattice parameter b), and $23.1 \times 10^{-6} \text{ K}^{-1}$ (lattice parameter c). The mean values of the respective CTEs are $-2.2 \times 10^{-6} \text{ K}^{-1}$ (30 °C–300 °C) and $0.9 \times 10^{-6} \text{ K}^{-1}$ (30 °C–800 °C). These values are below those of the Ge-free compound Ba_{0.5}Sr_{0.5}Zn₂Si₂O₇ and also

below the values of most compositions where Zn^{2+} is replaced by other divalent transition metal ions or Mg^{2+} exhibiting the same crystal structure [9].

This should make such materials extremely resistant to thermal shock. However, obtaining a densely sintered material from such a highly anisotropic phase needs special techniques, such as sol-gel synthesis, in order to get crack-free materials [13]. If the Ge-concentration gets too high, the LT-modification becomes stabilized. In analogy, this can also be seen in the case of $\text{BaZn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ solid solutions, exhibiting generally the crystal structure of LT- $\text{BaZn}_2\text{Si}_2\text{O}_7$. These solid solutions show phase transitions to the HT-phase as illustrated in Figure 3. There it can be seen that an increasing Ge-concentration leads to an enlargement of the phase stability region of LT- $\text{BaZn}_2\text{Si}_2\text{O}_7$, i.e., a shifting of the phase transition to higher temperatures, which is also observed for compounds in which the Zn^{2+} -sites are substituted [2]. Further studies will be focused on the crystallization of phases with negative thermal expansion in order to achieve zero thermal expansion at room temperature and elevated temperatures.

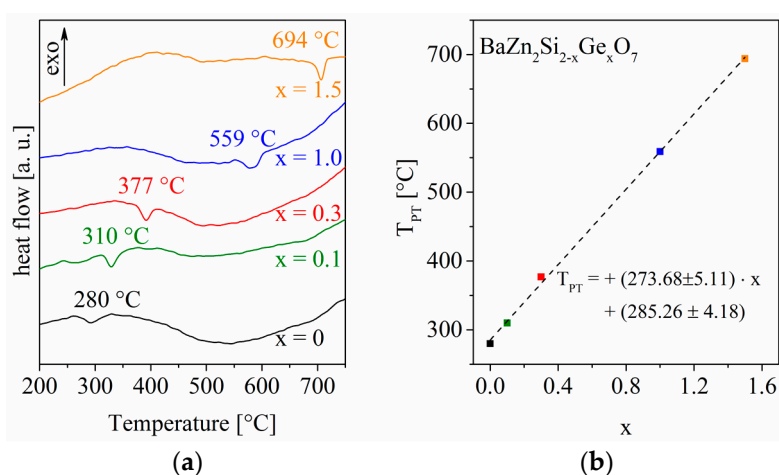


Figure 3. Phase transition temperatures T_{PT} of $\text{BaZn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ solid solutions with different values of x . (a) the DSC curves are illustrated together with the respective onset temperatures of the phase transition; (b) the phase transition temperatures are plotted in dependence of x . The linear regression (dashed line and formula) is also inserted.

3. Materials and Methods

Solid solutions within the series $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ and $\text{BaZn}_2\text{Si}_{2-x}\text{Ge}_x\text{O}_7$ were prepared with different values of x from stoichiometric mixtures of SiO_2 (>99%, Carl Roth GmbH & Co. KG, Karlsruhe, Germany), ZnO ($\geq 99\%$, Carl Roth GmbH & Co. KG), BaCO_3 (pure, VK Labor- und Feinchemikalien, Dresden, Germany), SrCO_3 (purest, Ferak, Berlin, Germany), and GeO_2 (>99.98%, ABCR GmbH & Co. KG, Karlsruhe, Germany). The respective powders were thoroughly mixed and afterwards heat treated at temperatures in the range from 1100 to 1200 °C kept for 20–30 h with several intermediate regrinding steps. Phase transition temperatures of the final powders were determined with differential scanning calorimetry DSC (LINSEIS DSC PT-1600, Selb, Germany). The phase analysis was performed with a SIEMENS D5000 Bragg-Brentano diffractometer (München, Germany) and $\text{Cu K}\alpha$ radiation. The thermal expansion of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_2\text{SiGeO}_7$ was determined up to 1000 °C with the same device equipped with an ANTON PAAR HTK 10 heating stage (Graz, Austria). For this purpose, the powdered samples were mixed with corundum in order to correct the height changes caused by the sample holder. Afterwards, the sample holder was heated with 5 K/s to the respective temperature. After a temperature equilibrium was reached, the scan was performed in the 2θ -range from 10° to 60° using an increment of $\Delta 2\theta = 0.02^\circ$. From the positions of the peaks, the lattice parameters were calculated with the software TOPAS 3 from BRUKER (Billerica, MA, USA).

4. Conclusions

The substitution of Si by Ge in HT- and LT-BaZn₂Si₂O₇ polymorphs generally leads to the stabilization or the enlargement of the phase stability region of the LT-phase. In the case of Ba_{0.5}Sr_{0.5}Zn₂SiGeO₇, the HT-phase is still stable and the introduction of Ge decreases the CTE so that overall negative thermal expansion was measured with HT-XRD. That means, in the family of Ba_{1-x}Sr_xZn_{2-y}M_ySi₂O₇ also the Si position, and hence all cationic positions can be substituted and nevertheless, negative thermal expansion can be achieved.

Author Contributions: C.T. and C.R. conceived and designed the experiments; C.T. performed the experiments; C.T. analyzed the data; C.T. and C.R. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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