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Investigations related to the incorporation of Ca^{2+} ions into the $BaTiO_3$ lattice

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Dependence of the composition of (100–x) $BaTiO_3$ + $x CaTiSiO_5$ precursor (x = 2–16 mol%) mixtures on calcination temperature was investigated by means of X-ray diffraction and differential scanning calorimetry. The formation of a secondary phase, fresnoite ($Ba_2TiSi_2O_8$), starts at about 900 °C. The resulting Ba and O vacancies and the produced microstress stabilize the pseudocubic phase of $BaTiO_3$ at room temperature. Temperatures higher than 1200 °C are necessary to incorporate Ca ions into the $BaTiO_3$ crystals forming (Ba, Ca)TiO_3 solid solutions. As a result the lattice becomes free of tension and the $BaTiO_3$ based ceramics transform into thermodynamically stable tetragonal phases at room temperature.

1. Introduction

Improvement of the semiconductive properties of barium titanate ($BaTiO_3$) based ceramics using $(Ba_{1-x}Ca_x)TiO_3$ solid solutions is well known. Ca substitution homogenizes the microstructure and increases the withstanding voltage of the ceramics. The effect of Ca substitution is differently discussed in the literature. It depends on the amount and source of the Ca^{2+} added. Kolar and Trontelj [1] report a maximum median grain size of the ceramics at a Ca content of 8 mol % using $CaTiO_3$ as the Ca source. No granulometric characteristics of the $CaTiO_3$ powder are given. If $CaCO_3$ is mixed with $BaCO_3$ and TiO_2 before calcination a decreasing grain size is observed with increasing Ca content, up to 16 mol % [2]. Tiwari *et al.* [3] found out that there is no significant influence of Ca content, ranging from 4–20 mol %, on the microstructure of the ceramics if a $(Ca_aBa_{1-a})CO_3$ solid solution is used as the starting material.

In all of these investigations the influence of calcium in the fired ceramics was considered only, no work was done in regard of the incorporation of Ca ions into the $BaTiO_3$ lattice. The aim of the present paper is to investigate the mechanism of incorporation of Ca ions into the $BaTiO_3$ lattice in the system $BaTiO_3$/ $CaTiSiO_5$ precursor as a function of calcination temperature.

2. Experimental procedure

2.1. Sample preparation

The samples were prepared by wet milling of a base powder, $Ba_{0.998}TiO_3 \cdot 0.001La_2O_3$ (in the text only written as $BaTiO_3$) and a $CaTiSiO_5$ precursor, (Ti–O–, Si–O-hydrogel + $Ca(OH)_2$ (hereafter referred to as $CaTiSiO_5$) [4], with agate balls in a PVC poly vinyl chloride drum for 24 h. The as-prepared mixtures were filtered and dried and then calcined in air for a soaking time of 2 h at the given temperature. The characterization was performed after cooling to room temperature.

The base powder was prepared by the ceramic mixed oxide method using $BaCO_3$ p.a. (Leuchtstoffe und Feinchemikalien GmbH, Bad Liebenstein), TiO_2 (Merck 808) and $La_2(C_2O_4)_3 \cdot 9H_2O$ (Stickstoffwerke Piesteritz) as starting materials and calcining the mixture 2 h at 1100 °C in air.

2.2. Powder characterization

2.2.1. *X-ray diffraction (XRD)*

The calcined powder mixtures were characterized by XRD using a Siemens D500 diffractometer operating with CuK_α radiation in a continuous scan mode, with a scan width of $2\Theta = 0.02°$ and a registration rate of $2\Theta = 0.5° \text{ min}^{-1}$. DIFFRAC 5000 was used as software for the peak profile fitting (regular Pearson VII) and for the determination of the full width at half maximum (FWHM) of the diffraction peaks. The α_1/α_2 splitting was considered. The FWHM was corrected by an empirically determined instrumental line broadening. The (0 0 2) and (2 0 0) reflections were mainly studied. In addition these reflections are an indicator of the phase transformation.

2.2.2. *Differential scanning calorimetry (DSC)*

The caloric measurements were performed with a DSC 200 (Fa. Netzsch) in the temperature range – 120 to + 200 °C with a heating rate of 10 K min^{-1} in air. An empty Al crucible was used as reference.

Dedicated to Professor Kurt Issleib on the occasion of his 75th birthday.

Liquid nitrogen was used for cooling. The measurements were repeated two-fold at least.

Barium titanate ($BaTiO_3$) undergoes several enantiotropic phase transitions with temperature. The change from the orthorhombic to the tetragonal phase ($T_{o/t}$ = 15 °C)* shows the strong dependence of transition temperature with Ca content in (Ba, Ca)TiO_3 [5]. This temperature shifting was used as an indicator of Ca incorporation into the $BaTiO_3$ lattice.

3. Results
3.1. XRD investigations

Fig. 1 shows the X-ray diffractograms of the 92 mol % $BaTiO_3$ + 8 mol % $CaTiSiO_5$ precursor mixture calcined at different temperatures. In the mixed and non-calcined powder, the (0 0 2) and (2 0 0) reflections of the tetragonal phase of $BaTiO_3$ are sharply separated. The intensity ratio is nearly 1 : 2. The separation decreases with increasing calcination temperature (900–1100 °C), and at 1200 °C only one broad signal is found.

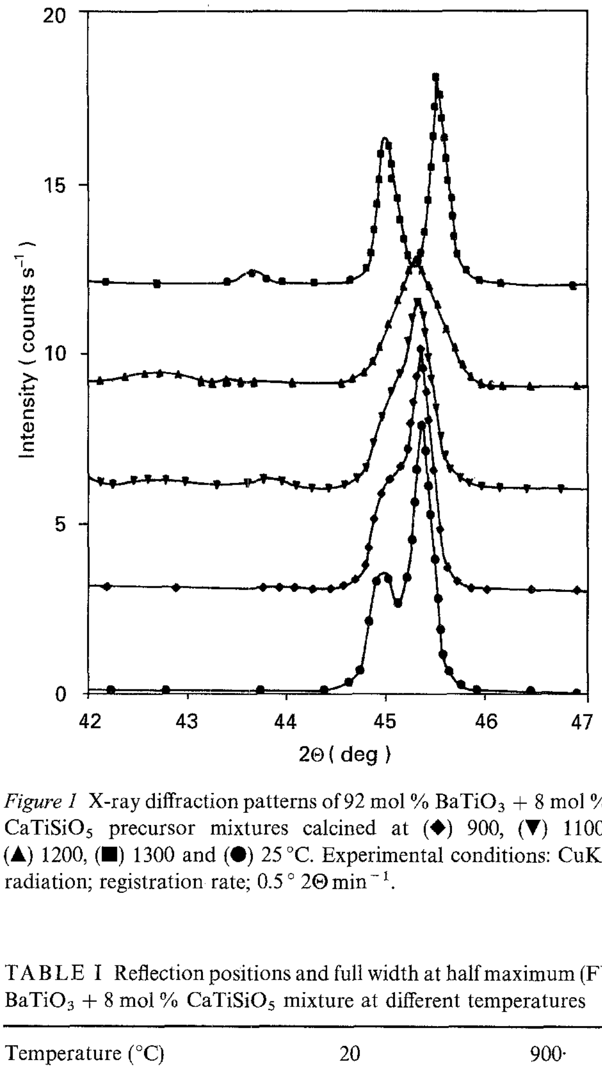

Figure 1 X-ray diffraction patterns of 92 mol % $BaTiO_3$ + 8 mol % $CaTiSiO_5$ precursor mixtures calcined at (◆) 900, (▼) 1100, (▲) 1200, (■) 1300 and (●) 25 °C. Experimental conditions: CuK_α radiation; registration rate; 0.5 ° 2Θ min^{-1}.

For a detailed investigation of this experimental finding, modelling of three peaks, was carried out, two of tetragonal phase [(0 0 2) and (2 0 0)] and one of pseudocubic phase (2 0 0) . The as-received peak positions and the FWHM are summarized in Table I. In general it can be stated that modelling using the additional pseudocubic phase peak leads to better reliability (Fig. 2a, b). The horizontal curve in the middle of the figure shows the deviation of the calculated values from the experimental ones.

It is interesting that even the $BaTiO_3$ starting powder exhibits small parts of the pseudocubic phase. This was also observed for Nd [6] and La [7] doped $BaTiO_3$ ceramics. The portion of the pseudocubic phase increases slightly by wet milling and mixing with the additive component. The reason for this could be mechanical activation and dissolvation of Ba^{2+} ions out of the lattice [8]. The position of the pseudocubic peak (Table I) received from the modelling is in good agreement with the value of $2\Theta = 45.202$, which was calculated from the lattice parameter $a_{o,c}$ = 0.400 86 nm, taking into account an equal volume of the tetragonal and the pseudocubic unit cell. ASTM card No. 31–174 gives the lattice parameter of the cubic modification, which was prepared by a wet chemical route. Therefore, these materials contain about 6% lattice-expanding components (for example HO^- groups) and a_o is given as 0.4031 nm. The position of the (0 0 2) reflection shifts to higher values of 2Θ, that of the (2 0 0) reflection of the tetragonal phase shifts to lower values of 2Θ with increasing calcination temperature up to 1200 °C. As a consequence the lattice parameters ratio, $c_{o/t}/a_{o/t}$, changed from 1.0095 at 20 °C to 1.0081 at 1100 °C. The FWHMs of both reflections increase. An increase in FWHM can be caused by the reduction of crystallite size and/or by microstress. The crystallite size does not change significantly in the system at temperatures reported above. Therefore, microstress ought to be the reason for the increase in FWHM. The FWHM of the

TABLE I Reflection positions and full width at half maximum (FWHM) calculated from the modelling of X-ray diffractograms of 92 mol % $BaTiO_3$ + 8 mol % $CaTiSiO_5$ mixture at different temperatures

Temperature (°C)	20	900	1100	1200	1300
Tetragonal reflection (0 0 2)					
Position, 2Θ	44.901	44.927	44.943	45.011	44.960
FWHM, 2Θ (deg)	0.102	0.152	0.124	0.246	0.073
Tetragonal reflection (2 0 0)					
Position, 2Θ	45.352	45.346	45.326	45.503	45.493
FWHM, 2Θ (deg)	0.065	0.069	0.105	0.192	0.045
Cubic reflection (2 0 0)					
Position, 2Θ	45.196	45.178	45.140	45.268	45.287
FWHM, 2Θ (deg)	0.253	0.202	0.227	0.250	0.105
Ratio of intensities					
$(2 0 0)_t : (2 0 0)_c$	2.83:1	2.21:1	1.6:1	0.32:1	11.6:1

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* It should be mentioned that one will find different transition points data in the literature.

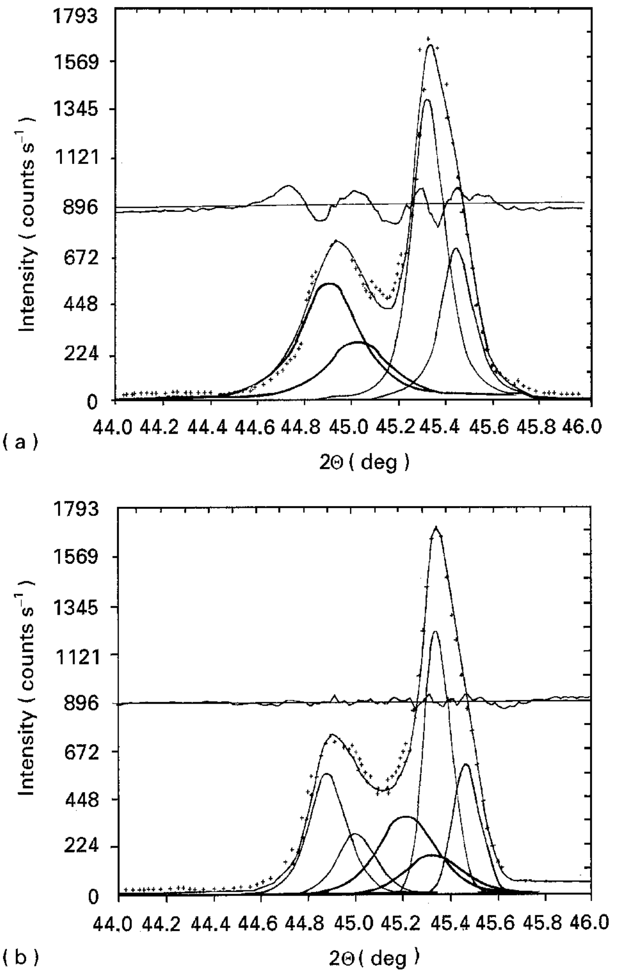

Figure 2 Measured (+) and calculated (–) graphs of the (0 0 2) and (2 0 0) reflections of $BaTiO_3$ calcined at 1100 °C, for 2 h, modelled with two peaks of the tetragonal phase (a), and with two peaks of the tetragonal phase and one of the pseudocubic phase (b). The horizontal line in the middle of the figure shows the deviation of the calculated values from the experimental ones. Experimental conditions: CuK_α radiation; registration rate, 0.5° 2Θ min^{-1}.

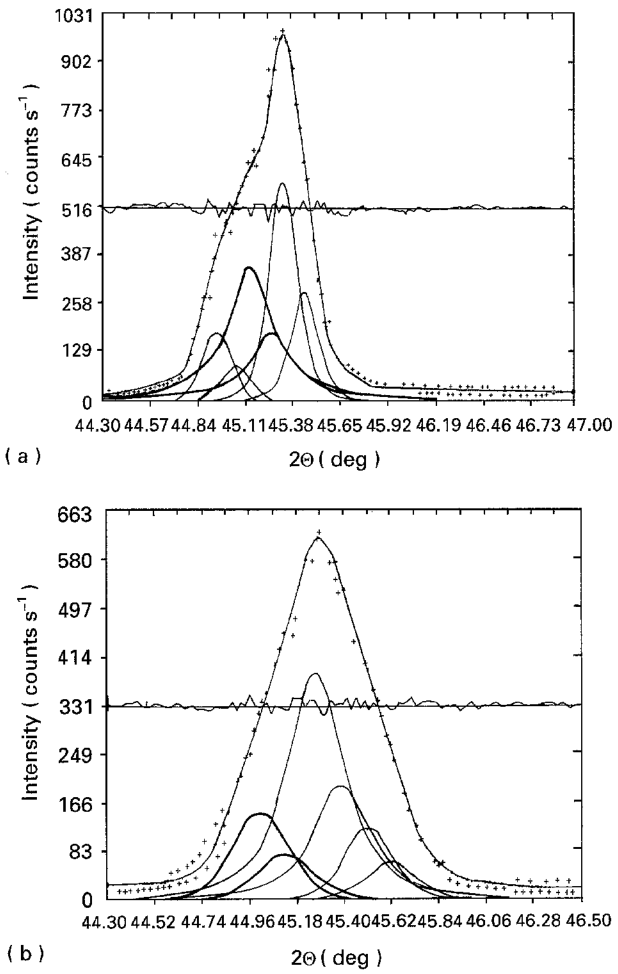

Figure 3 Measured (+) and calculated (–) graphs of the (0 0 2) and (2 0 0) reflections of $BaTiO_3$ resulting from 92 mol % $BaTiO_3$ + 8 mol % $CaTiSiO_5$ mixtures calcined at 1100 °C for 2h (a), and 1200 °C for 2h (b), modelled with two peaks of the tetragonal phase and one of the pseudocubic phase. Experimental conditions: CuK_α radiation; registration rate, 0.5° 2Θ min^{-1}.

(2 0 0) reflection of the pseudocubic phase is nearly constant with increasing temperature. Relation of the intensities of the (2 0 0) reflection of the tetragonal and pseudocubic phase shows a small, but continuous, variation (Table 1). After calcination at 1200 °C one has to ascertain a drastic drop of the intensity relation of the tetragonal and pseudocubic reflection from 1.6:1 at 1100 °C to 0.32:1 at 1200 °C (Table I, Fig. 3). The position of the modelled peaks shifts to higher 2Θ values.

The sample calcined at 1300 °C shows a pronounced grain growth. This is not unexpected because of the formation of a eutectic melt at 1250 °C in silica containing $BaTiO_3$ ceramics. (Ba, Ca) TiO_3 solid solutions free of microstress are formed via recrystallization and exist in the tetragonal modification after cooling below 120 °C. The positions of the reflections of the tetragonal phase correspond to the incorporation of Ca ions into the $BaTiO_3$ lattice. However, small pseudocubic parts still remain. Fresnoit ($Ba_2TiSi_2O_8$) forms as a secondary phase in the system $BaTiO_3$/$CaTiSiO_5$, beginning with a calcination temperature above about 900 °C. Under the conditions used neither the Ca stabilized $Ba_2Ti_5O_{12}$ [9] nor the $Ba_3Ca_2Ti_2O_9$ [10] phases have been observed in the examined range of temperature.

3.2. DSC investigations

(100–x)$BaTiO_3$ + $x$$CaTiSiO_5$ mixtures, with $x = 0$–16 mol %, were investigated. The as-received graphs are summarized in Fig. 4. The transition points from the orthorhombic to the tetragonal phase, $T_{o/t}$, are comparable with those reported in [5]. For $x = 16$ mol %, $T_{o/t} = -73.9$ °C was determined. The strong dependence on the Ca content is evident; but with increasing Ca content the phase transition becomes more and more diffuse.

In Fig. 5 graphs of the 92 mol % $BaTiO_3$ + 8 mol % $CaTiSiO_5$ mixture calcined at different temperatures are shown. The uncalcined starting mixture exhibits phase transition temperatures of 127 °C (tetragonal → cubic), 14 °C (orthorhombic → tetragonal) and – 70 °C (rhombohedral → orthorhombic), which are characteristic for pure $BaTiO_3$. The broad peaks are a result of the diffuse phase transition caused by lattice distortion. Pure $BaTiO_3$ was also measured after calcination of 5 h at 1350 °C (Fig. 6). The more ordered status is clearly seen by the sharpness of the peaks. The transition enthalpy determined in the interval 110–150 °C amounts to 189 J mol^{-1}, and is comparable with the value of 200 J mol^{-1} reported in [11, 12]. For the sample calcined 2 h at 1100 °C, the

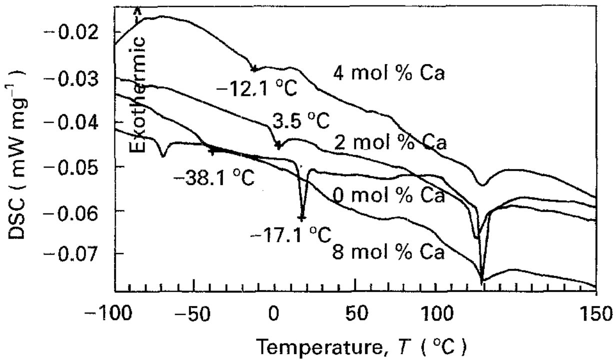

Figure 4 DSC investigations of (100–x) $BaTiO_3 + xCaTiSiO_5$ (x = 0–8 mol % mixtures calcined at 1300 °C for 2h. Experimental conditions: heating rate, 10 K min^{-1} in air.

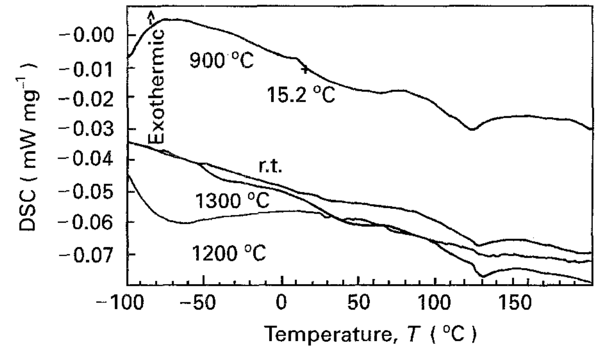

Figure 5 DSC investigations of 92 mol % $BaTiO_3$ + 8 mol % $CaTiSiO_5$ mixtures calcined at different temperatures. Experimental conditions: heating rate, 10 K min^{-1} in air.

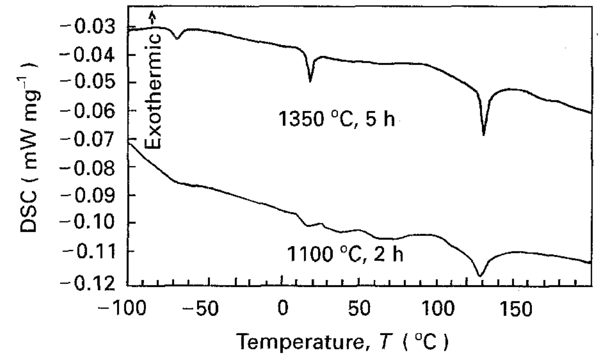

Figure 6 DSC investigations of $BaTiO_3$ powders prepared by the mixed oxide method calcined at different temperatures. Experimental conditions: heating rate, 10 K min^{-1} in air.

transition enthalpy was found to be 170 J mol^{-1}. The chemical analysis detects minimal amounts of unreacted $BaCO_3$ and BaO only. It is concluded therefore that pseudocubic $BaTiO_3$ is present in small amounts at room temperature.

The graph of the mixture calcined at 900 °C (Fig. 5) and that of the mixture calcined at 1100 °C (not shown in Fig. 5) are similar to that of the uncalcined powder. The transition point from orthorhombic to tetragonal $BaTiO_3$ was $T_{o/t}$ = 15 °C.

After calcination at 1200 °C no heat effects are detectable in the temperature region 100–150 °C. That means that the produced pseudocubic phase is stable even in the region of room temperature.

The mixture calcined at 1300 °C shows detectable phase transitions from orthorhombic → tetragonal ($T_{o/t} = -38$ °C) and from tetragonal → cubic ($T_{t/c}$ = 129 °C). The shifting of $T_{o/t}$ to lower values is an indicator of the substitution of Ca for Ba ions in the $BaTiO_3$ lattice.

Taking into account these experimental results variations in the structure of the matrix component in the $BaTiO_3/CaTiSiO_5$ system are discussed as a function of calcination temperature as follows.

Starting at around 900 °C fresnoit ($Ba_2TiSi_2O_8$) is formed from the added $CaTiSiO_5$ precursor and Ba and O ions from the matrix component. In the $BaTiO_3$ crystals Ba and O vacancies are left (Equation 1)

$$100 - xBaTiO_3 + xCaTiSiO_5 \rightarrow x/2\,Ba_2TiSi_2O_8 + aBaTiO_3 + b(V''_{Ba} + Ti_{Ti} + 2O_O + V_O^{\bullet\bullet}) + xCaO + cTiO_2 \qquad (1)$$

The $Ba_2TiSi_2O_8$ is unambiguously determined by XRD, whereas the existence of CaO, TiO_2 and $CaTiO_3$, respectively, is not detectable by this method. Also, the possible formation of TiO_2 rich phases, like $Ba_6Ti_{17}O_{40}$, could not be observed. The postulated vacancies are considered to be the reasons for the growing microstress, which results in stabilization of the quasicubic phase also at room temperature. One can discuss the same mechanism in [7, 8] for the increasing part of the cubic phase with increasing dopant concentration if one takes into account the assumption that the higher valent dopants are compensated by barium vacancies, V''_{Ba}. Criado [13] reports that the oxygen vacancies, $V_O^{\bullet\bullet}$, are the reason for the formation of small coherently diffracting domains and therefore for the stabilization of the cubic phase. The tendency of stabilization of the pseudocubic phase increases with increasing calcination temperature up to 1200 °C. Up to this temperature one cannot detect any substitution of Ca ions for Ba ions in the $BaTiO_3$ lattice in the DSC graphs. The lattice parameters decrease, but the reason is, in the authors' opinion, the formation of V''_{Ba} and $V_O^{\bullet\bullet}$ in the (h00) and the (001) planes. In the 1200 °C calcined samples the produced microstress is so strong that most of the $BaTiO_3$ remains in the pseudocubic modification after cooling down to room temperature. In the DSC graph there is no transition detectable from tetragonal to cubic modification.

Using a ceramic powder mixture of the cross composition 92 mol % $La_{0.002}Ba_{0.911}Ca_{0.087}Ti_{1.01}O_{3.02}$, in which Ca^{2+} is already incorporated into the $BaTiO_3$ lattice and 4 mol % $Ba_2TiSi_2O_8$ (wet chemical prepared [14]) is added, the changes of the (002) and (200) peaks are only very small in comparison to that discussed above. This means no Ba^{2+} nor O^{2-} ions are removed from the $BaTiO_3$ matrix to form $Ba_2TiSi_2O_8$ according to Equation 1. Therefore, the formation of barium and oxygen vacancies are not promoted.

At temperatures $T > 1250\,^{\circ}\mathrm{C}$ a eutectic is formed and "recrystallization" of the $\mathrm{BaTiO_3}$ matrix component proceeds. The vacancies are filled by Ca and O ions (Equation 2), the microstress is reduced and, therefore, stabilization of the pseudocubic phase is abolished.

$$x\mathrm{CaO} + a\mathrm{BaTiO_3} + b(V''_{\mathrm{Ba}} + \mathrm{Ti_{Ti}} + 2\mathrm{O_O} + V^{\bullet\bullet}_{\mathrm{O}}) \rightarrow (\mathrm{Ba}_a\mathrm{Ca}_x)\mathrm{Ti}_{a+b}\mathrm{O}_{3a+2b+x} \quad (2)$$

The positions of the reflections in the X-ray diffractogram are shifted to higher values of 2Θ indicating the presence of $\mathrm{(Ca, Ba)TiO_3}$ solid solutions.

When the investigations are carried out with a Ca free Ti-Si-O-hydrogel instead of $\mathrm{CaTiSiO_5}$, the same tendencies are observed with respect to the XRD and DSC results depending on the calcination temperature. Above a calcination temperature of 1300 °C, the XRD spectra indicate the presence of a tetragonal phase after cooling at room temperature again and in addition the presence of $\mathrm{Ba_6Ti_{17}O_{40}}$. In this case the intermediately appeared vacancies and microstress will be reduced by the formation of $\mathrm{TiO_2}$ rich phases.

4. Conclusions

Si containing secondary phases stabilize the pseudocubic phase of $\mathrm{BaTiO_3}$ at room temperature depending on the calcination temperature. In the presence of $\mathrm{Ca^{2+}}$ the formation of $\mathrm{(Ca, Ba)TiO_3}$ solid solutions starts at about 1200 °C. The content of the pseudocubic phase increases with increasing calcination temperature until about 1200 °C; whereas at 1300 °C, the tetragonal phase at room temperature is detected only. In order to explain this behaviour, the origin of microstress arising from barium and oxygen vacancies was discussed, which resulted during the formation of $\mathrm{Ba_2TiSi_2O_8}$. Varying the temperature of heat treatment, the content of pseudocubic $\mathrm{BaTiO_3}$ is adjustable.

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