CHEMICAL REACTIONS BETWEEN BaTiO₃ CERAMICS AND FLUORINE-CONTAINING ATMOSPHERE[†]

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[†]This paper is dedicated to the late Dr. Karel Lutar

Abstract

BaTiO₃ ceramics were exposed to fluorine-containing atmosphere prepared by introducing a fluorination agent (CF_3CH_2OH) into a hot alumina-tube furnace. The fluorinated samples were studied using SEM and TEM. The fluorination resulted in the formation of a surface-reaction layer with a complex structure. At the reaction front fluorine reacts with BaTiO₃ to produce BaF_2 and $BaTi_2O_5$. During the course of the fluorination the $BaTi_2O_5$ reacts further to produce BaF_2 and then subsequently Ba-polytitanates with an increasing content of titanium, and finally TiO_2. Fluorine also diffuses along the grain boundaries towards the pellet's interior. The presence of the fluorine stabilises the $BaTi_2O_5$ compound and consequently triggers its formation in the ceramic's interior in a reaction between BaTiO₃ and the intergranular phase $Ba_6Ti_{17}O_{40}$.

Introduction

The functional properties of ferroelectric BaTiO₃ ceramics can be tailored by doping with aliovalent dopants. By using low concentrations, BaTiO₃ ceramics can be prepared in the semiconducting state, even when sintering in air, and when subjected to exaggerated (anomalous) grain growth.[1] Usually, 3-valent ions substituted for Ba (La^{3+}, Ce^{3+}, Nd^{3+}, etc) or 5-valent ions substituted for Ti (Nb^{5+}, Sb^{5+}, etc) serve as the donor dopants. The semiconductivity of donor-doped BaTiO₃ is a consequence of the electronic compensation of excess donor charge, which can also be represented as the reduction of Ti^{4+} to Ti^{3+}, according to the solid-solution formula:

$Ba_{1-X}La^{\bullet}{}_{X}Ti^{4+}{}_{1-X}Ti^{3+}{}_{X}O_3$. Such semiconducting, donor-doped $BaTiO_3$ ceramics display a positive temperature coefficient of resistivity (the PTCR effect) – a sudden increase in resistivity near to the ferroelectric-to-paraelectric transition temperature (T_C). The PTCR effect is the basis for various technical applications, which use these materials in current limitors, self-regulating heating elements, television degaussers, etc.[2]

The PTCR effect in $BaTiO_3$ ceramics originates in the temperature-dependent potential barriers at the grain boundaries.[3] These potential barriers are formed by the creation of acceptor states at the surfaces of semiconducting, donor-doped $BaTiO_3$ grains. Usually, acceptor states, adsorbed oxygen[4] and/or intrinsic cation vacancies[5] are formed during the cooling of the ceramics from the sintering temperature in air by the preferential reoxidation of the grain boundaries.

Undoped $BaTiO_3$ can also be prepared in a semiconducting state, simply by atmospheric reduction ($BaTi^{4+}{}_{1-X}Ti^{3+}{}_{X}O_{3-X/2}(V^{\bullet\bullet}{}_O)_{X/2}$). Due to the high concentration of the oxygen vacancies in the lattice of the matrix grains it is practically impossible to provoke a significant PTCR effect in atmospherically reduced $BaTiO_3$ ceramics by preferential reoxidation of the grain boundaries. However, Alles et al.[6] showed that the PTCR effect could be provoked in undoped, atmospherically reduced $BaTiO_3$ ceramics exposed to a fluorine-containing atmosphere. They suggested that the fluorine adsorbed at the grain boundaries serves as the acceptors needed for the PTCR effect.

On the other hand, the fluorine (F^{1-}) incorporated into the $BaTiO_3$ perovskite structure in the oxygen (O^{2-}) sub-lattice would act as the donor dopant. The substitution of O^{2-} ions with F^{1-} ions is to be expected since both ions have similar ionic radii.

In the present work the chemical reactions of undoped $BaTiO_3$ ceramics with a fluorine-containing atmosphere were studied using electron microscopy (SEM, TEM).

Experimental

The pellets of $BaTiO_3$ ceramic (~ 8-mm diameter and ~ 2-mm high) were prepared by sintering $BaTiO_3$ with an excess of 2 mol % TiO_2 at 1360 ^{o}C for 6 hours in air. The pellets were exposed to a fluorine-containing atmosphere for 2 hours at 900 ^{o}C. A flow of nitrogen supporting gas, bubbling through a fluorination agent (2,2,2-Trifluoroethanol = CF_3CH_2OH), was introduced into the hot alumina-tube furnace. The concentration of

the fluorination agent in the inlet atmosphere was determined with mass spectrometry to be approximately 0.5 %. The fluorination agent decomposes at high temperatures forming HF, which reacts with the $BaTiO_3$ pellets. No products of the fluorination-agent decomposition could be detected in the outlet atmosphere by mass spectrometry, suggesting that they were all consumed by chemical reactions inside the furnace.

Annealing the $BaTiO_3$ pellets in the fluorine-containing atmosphere resulted in the formation of a surface-reaction layer. For the SEM analysis a cross-section of the $BaTiO_3$ pellets with a reaction layer were prepared using standard metallographic methods. The surface-reaction reaction layer was analysed using a combination of SE/BE imaging and (semi-quantitative) EDXS analyses in a SEM (Model JSM 5800, JEOL, Tokyo, Japan) equipped with a LINK ISIS EDXS 300 analyser. Quantification[7] was performed with Oxford ISIS software using a library of virtual standards.

Using the TEM, the interiors of the fluorinated $BaTiO_3$ pellets were also in addition to the reaction layers formed at their surfaces. To prepare the cross-section of the surface region of the pellet with the reaction layer, two pellets were glued together using an epoxy resin. From the pair of glued pellets, a cylinder of material was cut parallel to the reaction layers. The cylinder with two surface-reaction layers in the middle of the ceramic material was then mounted in a metal tube and cut into the thin slices perpendicularly to the reaction layers. From the slices 3-mm-diameter discs were cut with the cross-section of the surface-reaction layers in the middle. At the centre of the disc a region about 20-µm thick was then produced with a dimple grinder. Finally, the specimens were thinned using argon-ion erosion at 4 kV with an incident angle of about 10° to make them transparent for the electron beam.

The reaction products of the fluorination were studied using BF and DF imaging in the combination with electron diffraction (SAED) and EDXS analysis using a TEM (Model JEM 2000 FX, JEOL, Tokyo, Japan) operating at 200 kV.

One of the products of the fluorination was the compound $BaTi_2O_5$. In order to verify the possible mechanism of its formation, mixtures of $BaCO_3$, BaF_2 and TiO_2 were prepared with a fixed barium-to-titanium atomic ratio equal to 0.5 and different contents of BaF_2 from 0 to 10 mol.%. The mixtures were annealed for a long time of 15 hours at

1100 ^{o}C in a flow of nitrogen that was dried using molecular sieves. The dry atmosphere was used to prevent the possible hydrolysis of the fluorite.

Results and discussion

The as-sintered ceramics were dense without any open porosity. The microstructures consisted of $BaTiO_3$ matrix grains, approximately 30 μm in size, and an intergranular phase, $Ba_6Ti_{17}O_{40}$, situated preferentially at the triple points that are formed with the crystallisation of the Ti-rich liquid phase.

As a result of the surface reaction of the $BaTiO_3$ pellets with the fluorine-containing atmosphere a dense surface-reaction layer was formed. However, the electrical properties,[8] as well as the microstructural features strongly suggested that fluorine also diffused into the pellet interior.

1. Surface reactions of BaTiO$_3$ ceramics with fluorine-containing atmosphere

Fig.1 is a SEM back–scattered image (BEI) of the reaction layer formed by a surface reaction during the exposure of the $BaTiO_3$ ceramics to the fluorine–containing atmosphere for 2 hours at 900 ^{o}C. The dense reaction layer has a complex structure which may be divided into three regions:

The region of the reaction layer near to the surface is enriched in barium and fluorine. Two phases could be distinguished in this region: a semi-quantitative EDXS analysis of large (up to 10 μm), rounded grains (white in the BEI image) match with the composition of pure BaF_2, while the phase which appears grey in the BEI image (marked by **X**) contains, in addition to barium and fluorine, also titanium and oxygen. An EDXS analysis showed that the atomic ratio of barium to titanium in this phase is roughly 2 : 1 (Because of the large error, quantification of the analysis of the two light elements, oxygen and fluorine, was not possible in this case).

The region in the middle of the reaction layer is enriched in titanium. It is composed of small, elongated, white grains, intermixed with dark needle-like crystals. Only the larger grains of two the phases in that region of the reaction layer were large enough for

EDXS analysis in the SEM, which proved the presence of BaF_2 (white in the BEI image) and TiO_2 (dark in the BEI image).

Near to the reaction front (marked in Fig.1 by **RF**) a relatively homogeneous region is present, which is composed of barium, titanium, oxygen and fluorine. Semi-quantitative EDXS analysis showed that the atomic ratio between barium and titanium is approximately 1 : 1. The reaction front, which moved with time from the surface of the pellet towards its interior, skipped the Ti-rich intergranular phase $Ba_6Ti_{17}O_{40}$ (see the nonreacted $Ba_6Ti_{17}O_{40}$ grain inside the reaction layer marked in Fig. 1 with **BT$_3$**), suggesting that this phase has a lower reactivity with fluorine than $BaTiO_3$.
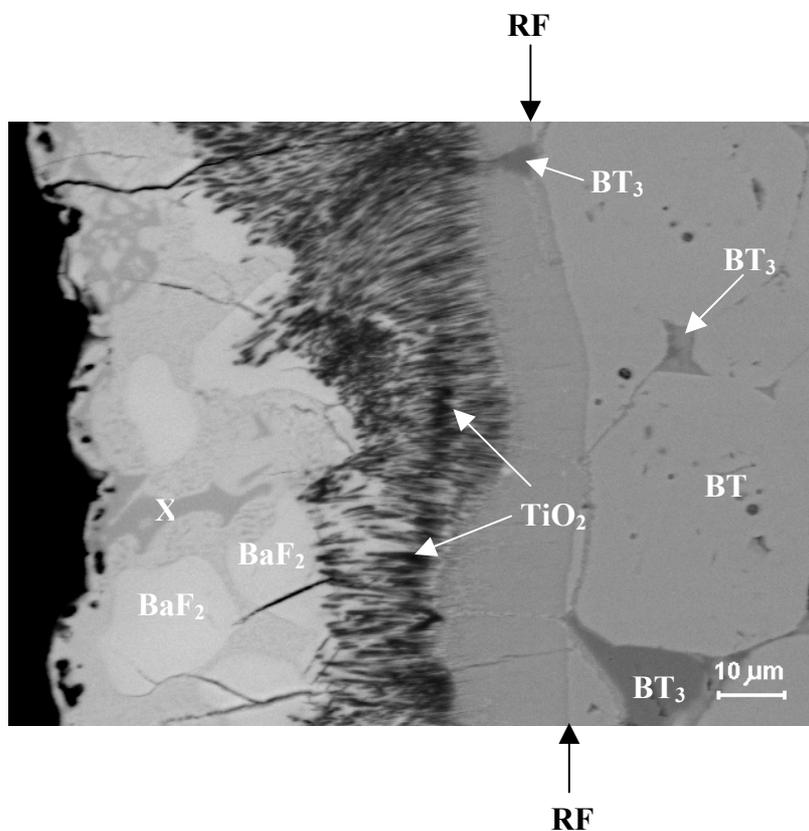

Fig. 1: A SEM back-scattered image (BEI) of the reaction layer formed by a surface reaction during exposure of the $BaTiO_3$ ceramics to the fluorine containing atmosphere for 2 hours at 900°C. (**BT** – $BaTiO_3$, **BT$_3$** – $Ba_6Ti_{17}O_{40}$, **X** – phase composed of Ba, F, Ti and O, **RF** – reaction front).

In the SEM BEI images (Figs. 1 and 2), the reaction layer near the reaction front seems homogeneous and single phase, even though the original boundaries of the reacted $BaTiO_3$ grains are enriched by BaF_2 (marked with **OGB** in Fig. 2). However,

TEM analysis proved that the reaction layer near the reaction front is actually a mixture of small grains of BaF_2 and different Ba-polytitanates.
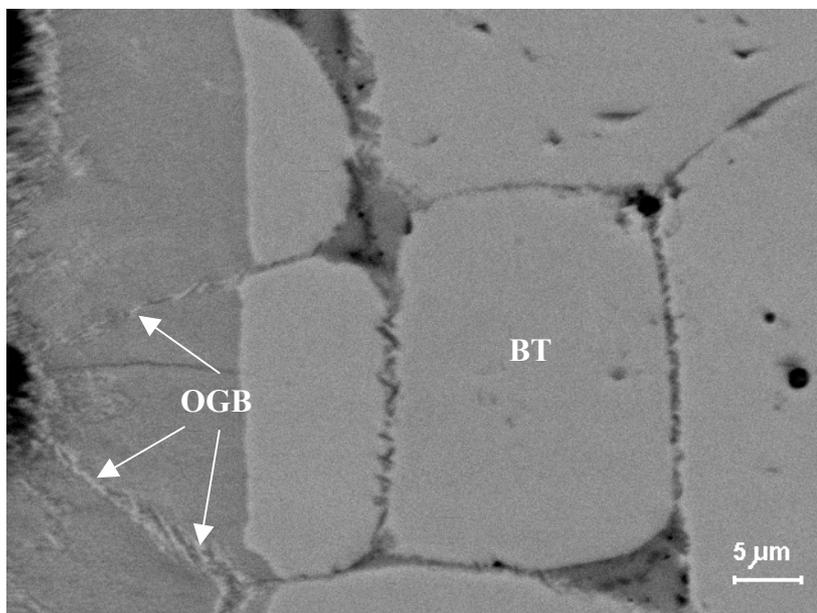

Fig. 2: A SEM back–scattered image (BEI) of the reaction layer near the reaction front formed by a surface reaction during exposure of the $BaTiO_3$ ceramics to the fluorine–containing atmosphere for 2 hours at 900 ^{o}C. (**OGB** – original grain boundary)

Fig. 3 shows the products of the fluorination reaction in contact with the $BaTiO_3$ (**BT**) grain. The corresponding electron diffraction patterns match with the fluorite structure of BaF_2 (cubic, a = 0.62 nm) and the monoclinic structure of $BaTi_2O_5$ (**BT$_2$)** (a = 0.9409 nm, b = 0.3932 nm, c = 1.6907 nm and β = 103.500 ^{o}).
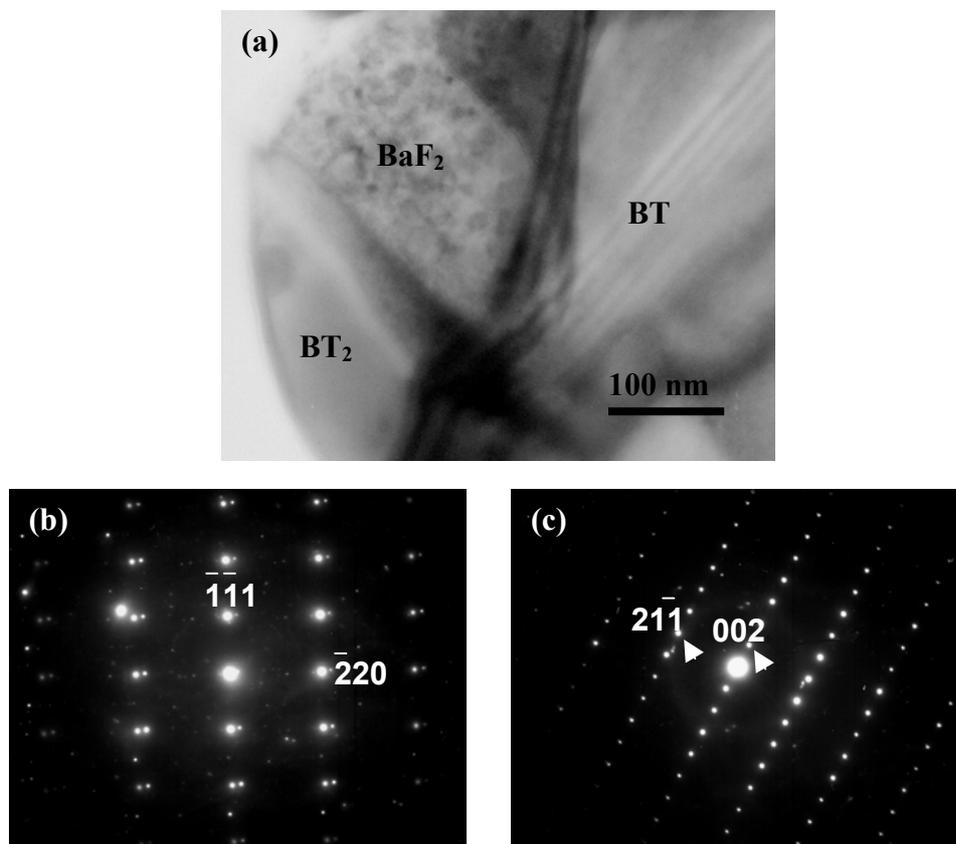
Fig. 3: TEM BF image of the products of fluorination at the reaction front (a) and electron diffraction patterns taken at the BaF_2 grain (b) (marked in Fig. 3 (a) with **BaF_2**, zone axis [112]) and at the grain of $BaTi_2O_5$ (c) (marked in Fig. 3 (a) with **BT_2**, zone axis [120]).

Fig. 4 is a TEM BF image of the reaction layer near to the reaction front showing a columnar-shaped BaF_2 grain surrounded by polytitanate grains. The columnar-shaped BaF_2 grain is oriented along the direction of the reaction-layer growth. Careful inspection of the electron diffraction patterns taken from polytitanate grains showed that, in this case, the polytitanate phase is the $Ba_2Ti_9O_{20}$ compound. Generally, the amount of Ti in the Ba-polytitanates in the reaction layer increases with the distance from the reaction front. Thus, Ba-polytitanate $BaTi_2O_5$ was present near to the reaction front, whereas at larger distances from the reaction front $Ba_6Ti_{17}O_{40}$, $Ba_4Ti_{13}O_{30}$ and $Ba_2Ti_9O_{20}$ were detected.
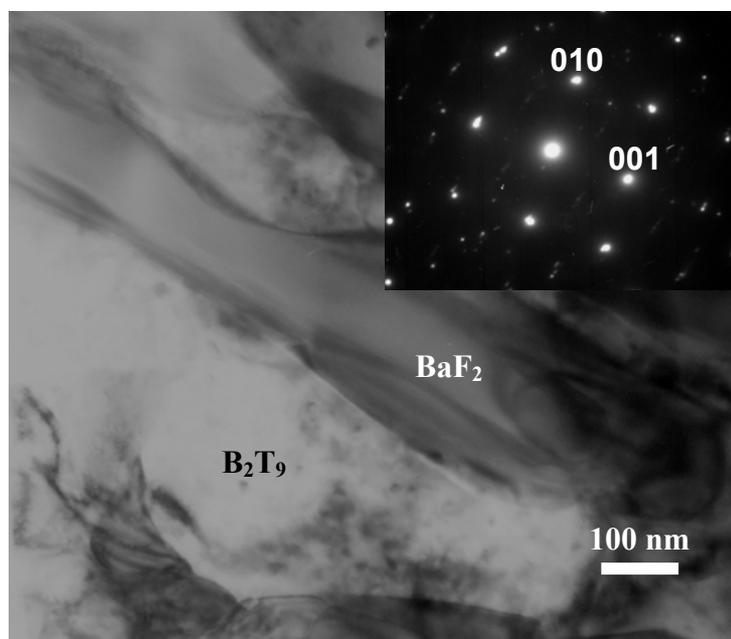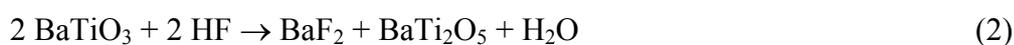
Fig. 4: TEM BF image and the corresponding electron diffraction pattern along [100] (inset) of the columnar-shaped BaF_2 grain in the matrix of Ba-polytitanate grains. The micrograph was taken from the region of the specimen with the reaction layer near the reaction front. (**B_2T_9** – $Ba_2Ti_9O_{20}$)

The final products of surface reactions between the $BaTiO_3$ ceramics and the fluorine–containing atmosphere are BaF_2 and TiO_2, according to the following chemical reaction:

$$BaTiO_3 + 2\,HF \rightarrow BaF_2 + TiO_2 + H_2O \tag{1}$$

At the reaction front the fluorine reacts with the Ba from the $BaTiO_3$ producing BaF_2 and a Ba-polytitanate phase with the lowest content of Ti, i.e. $BaTi_2O_5$[9]:

$$2\,BaTiO_3 + 2\,HF \rightarrow BaF_2 + BaTi_2O_5 + H_2O \tag{2}$$

The composition of the Ba-polytitanate phase changes during the course of the fluorination in a number of steps from $BaTi_2O_5$ at the reaction front, through Ba–polytitanates containing more Ti, and finally to pure TiO_2.

The surface reactions are controlled by the diffusion of the ions through the reaction layer. Based on the distribution of different phases across the reaction layer we concluded that fluorine diffuses from the surface towards the samples' interior, while barium and oxygen ions counter–diffuse towards the surface. Titanium is concentrated in the middle of the reaction layer. Thus, the BaF_2 product is concentrated near the surface and the TiO_2 is in the middle of the reaction layer.

2. Reactions in the interior of the $BaTiO_3$-ceramic pellet

Apart from surface reaction, the chemical reactions caused by fluorination can also be observed at the boundaries between the $BaTiO_3$ grains that are behind the reaction front. The change in the $BaTiO_3$ grain-boundary morphology can be observed in the region of the pellet near the reaction front (Fig. 2), suggesting that fluorine diffuses along the grain boundaries of the $BaTiO_3$ ceramics. Using the SEM, such an influence of fluorination on the grain-boundary morphology could not be observed in the centre of the pellet. However, using TEM, the chemical reactions occurring at the grain boundaries in the centre of the $BaTiO_3$ pellet could be observed.

The specimens for the TEM analyses were prepared from material cut from the centre of the pellet. Fig. 5 is a BF TEM image of the $BaTi_2O_5$ grains (**BT$_2$**), grown at the interface between the $BaTiO_3$ (**BT**) grain and the solidified liquid phase $Ba_6Ti_{17}O_{40}$ (**BT$_3$**). $Ba_6Ti_{17}O_{40}$ was already present at the grain boundaries of the as-sintered $BaTiO_3$ ceramics, while $BaTi_2O_5$ formed during the fluorination. An analysis of the electron diffraction patterns showed that most of the $BaTi_2O_5$ grains analysed have a particular orientation with respect to their neighbouring $BaTiO_3$ grain.
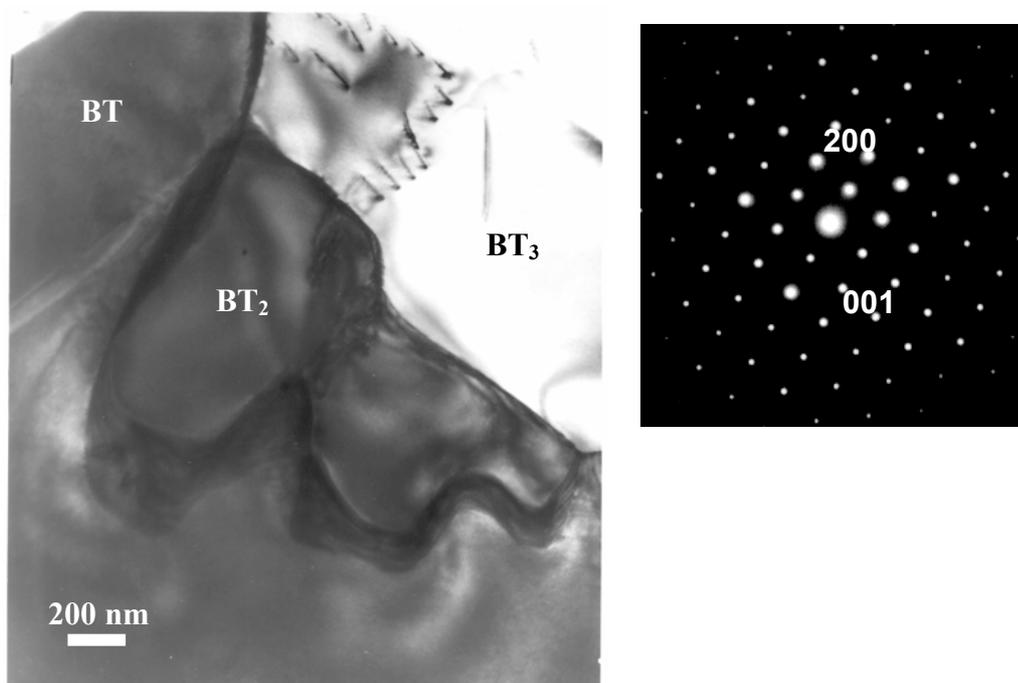
Fig. 5: TEM BF image (a) and corresponding electron diffraction pattern (zone axis [010]) (b) of the $BaTi_2O_5$ product (denoted as **BT₂**) at the interface between a $BaTiO_3$ grain (**BT**) and the intergranular phase $Ba_6Ti_{17}O_{40}$ (**BT₃**) in the interior of the fluorinated pellet

BaF_2 was never detected in the interior of the pellet. Moreover, using EDXS and TEM, fluorine could not be detected anywhere inside these samples. Here, it should be noted that in this case the detection limit for fluorine as a light element in a matrix of heavier elements, barium and titanium, is relatively high.

In order to test whether the $BaTi_2O_5$ appeared as a consequence of the presence of the fluorine in the interior of the sample or for other reasons, the sintered $BaTiO_3$ pellets were heat treated in ethanol vapour under the same experimental conditions used during fluorination. When the fluorination agent CF_3CH_2OH was replaced with ethanol (CH_3CH_2OH), $BaTi_2O_5$ was never observed in the treated $BaTiO_3$ ceramics. This experiment strongly suggests that the appearance of the $BaTi_2O_5$ is related to the fluorination process.

The presence of the $BaTi_2O_5$, both in the reaction layer and especially in the interior of the fluorinated ceramics, is rather surprising. The $BaTi_2O_5$ phase is believed to be a metastable compound that only forms through an amorphous intermediate (melt or gel)[9]. This tends to imply that the $BaTi_2O_5$ compound is stabilised by the presence of the fluorine.

In order to prove that the presence of the fluorine stabilises the $BaTi_2O_5$ compound, the mixtures of $BaCO_3$, BaF_2 and TiO_2 with barium-to-titanium ratios equal to 0.5 but different contents of BaF_2 (0, 1, 5 and 10 mol.%) were annealed at 1100 ^{o}C in dry nitrogen. The sample without the BaF_2 and the one that contained 1 mol.% of BaF_2 were composed of two compounds, $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$, according to known phase relations in the $BaO–TiO_2$ system[9], while the samples containing 5 and 10 mol.% of BaF_2 were single-phase $BaTi_2O_5$ (Fig. 6). The experiment proves that the presence of fluorine stabilises the $BaTi_2O_5$ compound.
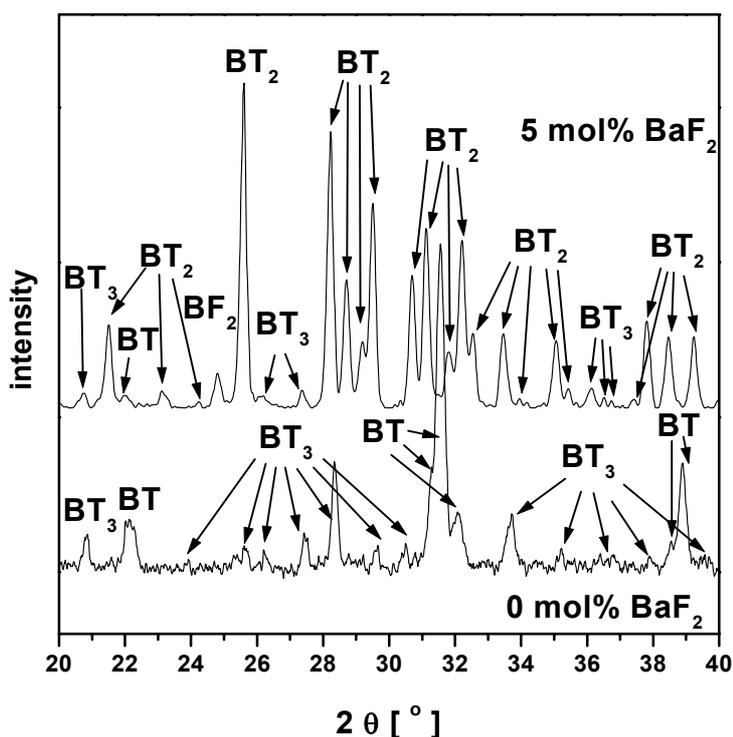

Fig. 6: X-ray diffractograms of the mixtures of $BaCO_3$, BaF_2 and TiO_2, with a barium-to-titanium ratio equal to 0.5 but different contents of BaF_2 (0 and 5 mol.%). The mixtures were annealed at 1100 ^{o}C in dry nitrogen. (**BT** - $BaTiO_3$, **BT$_3$** – $Ba_6Ti_{17}O_{40}$, **BT$_2$** – $BaTi_2O_5$, **BF$_2$** – BaF_2)

This stabilisation of the $BaTi_2O_5$ compound by the presence of fluorine could explain its appearance in the interior of the fluorinated pellets. Fluorine diffuses along the grain boundaries in the interior of the sample where it triggers the reaction between $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$:

$$5 \; BaTiO_3 + Ba_6Ti_{17}O_{40} \rightarrow 11 \; BaTi_2O_5 \hspace{3cm} (3)$$

Conclusions

The chemical reactions that occurred between the $BaTiO_3$ ceramics and the fluorine-containing atmosphere at high temperatures were studied using SEM and TEM techniques. The fluorination process resulted in the formation of a dense surface-reaction layer composed of different phases. The products of the fluorination surface reactions were BaF_2 and various Ti-rich phases. $BaTi_2O_5$ was formed at the reaction front, while during the course of the fluorination the composition of the Ti–rich phases changed in a number of steps from a Ba–polytitanate phase containing less Ti, through Ba–polytitanates containing more Ti, and finally to pure TiO_2.

The influence of fluorine was also detected in the interior of the $BaTiO_3$ ceramics. Here, the chemical reaction between $BaTiO_3$ and the intergranular phase $Ba_6Ti_{17}O_{40}$ occurred, resulting in the formation of $BaTi_2O_5$. This reaction occurred because the presence of fluorine stabilised the $BaTi_2O_5$ compound, which is metastable in the pure BaO–TiO_2 system.

Acknowledgements

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Povzetek

Keramiko BaTiO$_3$ smo izpostavili fluorovi atmosferi, ki smo jo pripravili z vpihovanjem fluorirnega sredstva (CF$_3$CH$_2$OH) v vročo cevno peč. Fluorirane vzorce smo analizirali z vrstično (SEM) in transmisijsko elektronsko mikroskopijo (TEM). Med fluoriranjem se je na površini keramike tvoril reakcijski sloj komplicirane strukture. Na reakcijskem čelu je fluor reagiral z zrni BaTiO$_3$ in nastajala sta BaF$_2$ in BaTi$_2$O$_5$. S časom fluoriranja je BaTi$_2$O$_5$ nadalje reagiral s fluorom v BaF$_2$ in različne Ba-polititanate z naraščajočo vsebnostjo titana, in končno v čisti TiO$_2$. Razen površinske reakcije keramike BaTiO$_3$ s fluorovo atmosfero smo opazili, da fluor prodira vzdolž mej med zrni proti notranjosti keramike. Prisotnost fluora v notranjosti keramike je stabilizirala fazo BaTi$_2$O$_5$ in tako sprožila njen nastanek z reakcijo med BaTiO$_3$ in intergranularno fazo Ba$_6$Ti$_{17}$O$_{40}$.