

BaTiO₃ Formation by Solid State Reactions on Rutile Single Crystals

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1. Introduction

During the synthesis of BaTiO₃ ceramics out of a stoichiometric BaCO₃-TiO₂ powder mixture, the evolution of different intermediate phases can generally be observed during the BaTiO₃-forming process [1]. These intermediate products are Ba₂TiO₄ and Ti-rich phases. When micro-chemically designed core-shell powders are used, the sequence of the forming phases changes, however [2]. To understand this behavior, model experiments are performed using rutile (TiO₂) single crystals with different surface orientations as one reactant. The solid-solid and gas-solid reactions of the latter with BaCO₃ (solid) and BaO (vapour), and the formation of a well-oriented BaTiO₃ phase are studied.

2. Experiment and results

A BaCO₃ target is e-beam evaporated in a high vacuum system with an oxygen background pressure of 1×10^{-2} Pa. The substrates are heated in a tube furnace from 300 °C to 500 °C during deposition, followed by solid-solid reaction at 575 °C to 900 °C between BaCO₃ and TiO₂ for 30 minutes in vacuum or in air, and from 575 °C to 900 °C during deposition for the gas-solid reaction. The reaction products are investigated by XRD and TEM.

A deposition at 500 °C followed by solid-solid reaction under vacuum at 600 °C for 30 minutes resulted in the formation of the metastable intermediate Ba₂TiO₄ phase, without any evidence of BaTiO₃ formation, while the solid-solid reaction in air resulted in the formation of BaTiO₃ (Fig. 1). To establish the prevailing diffusing direction, marker experiments were performed, using small Pt islands as inert markers. After deposition at 500 °C the Pt markers were found on a certain distance from the rutile surface (Fig. 2a). The Pt particles can be found on top of the reaction products after solid-solid reaction at 700 °C (Fig. 2b). The position of the Pt particles within the BaCO₃ phase (Fig. 2a) might result from out-diffusion of Ti ions, while their position on top of the thin film (Fig. 2b) can be explained by in-diffusion of Ba ions. For the gas-solid experiments a reaction process was found that is different from the observations in the solid-solid reaction. Reactions at 600 °C and 800 °C lead to the formation of BaTiO₃ and Ba₂TiO₄. A gas-solid reaction at 900 °C resulted in large pores between the substrate and the thin film. The film was converted almost completely to a Ti-rich phase, the latter being covered by the remaining BaTiO₃.

3. Conclusions

The present data show different rates of the solid state reactions and two different mass transport mechanisms. In the solid-solid reaction the mass transport mechanism takes place by grain boundary or bulk diffusion, and in the gas-solid reactions the basic mass transport mechanism is surface diffusion.

References

- [1] D. E. Rase, R. Roy, J. Amer. Ceram. Soc. 38, (1955) 102-113.
- [2] M. Rössel et al., Anal. Bioanal. Chem. 375, (2003) 310-314.

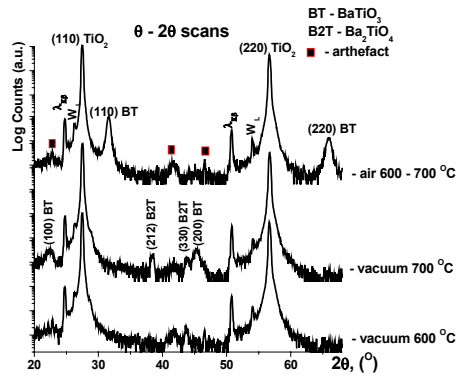


Fig. 1. XRD θ - 2θ solid reaction under

scans after solid-vacuum and in air.

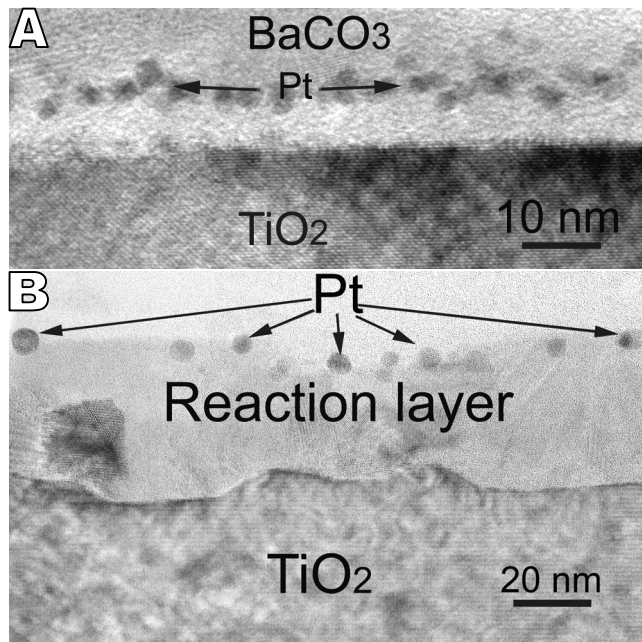


Fig.2. TEM images of the thin films after a) deposition of BaCO₃ at 500 °C and b) reaction at 700 °C with (110) TiO₂ substrate.