MITT.ÖSTERR.MINER.GES. 148 (2003)

CHEMICAL TRANSPORT REACTION STUDIES OF THE SYSTEM Sc_2O_3-Al_2O_3-TiO_2-SiO_2: GROWTH AND STRUCTURAL STUDIES OF SINGLE CRYSTALS OF MULLITE AND OTHER PHASES

U. Kolitsch[1], M. Weil[2] & E. Tillmanns[1]

[1]Institut für Mineralogie und Kristallographie
Universität Wien, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria
[2]Institut für Chemische Technologien und Analytik, Bereich Strukturchemie
Technische Universität Wien, Getreidemarkt 9/164-SC, A-1060 Wien, Austria

The system Sc_2O_3-Al_2O_3-TiO_2-SiO_2 contains several important binary ceramic phases, but the complete system is poorly known. Flux growth experiments in this system have yielded high-quality crystals of several oxidic Sc compounds by using various selected solvent mixtures [1-5], and have provided results on the apparent low-temperature instability of several Sc phases previously reported in this system. For comparison purposes, we have started studies of the phases and phase equilibria using the technique of chemical transport reactions [6] which are known to sometimes yield metastable phases. The studies of the system Sc_2O_3-Al_2O_3-TiO_2-SiO_2 were conducted in the overall temperature range 1100 $\rightarrow$ 950°C (endothermal transport), and were performed in sealed and evacuated silica glass ampoules which were filled with variable amounts of high-purity powders of the component oxides and the transport media. After run times of 7-10 d and quenching of the ampoules in cold water, runs with Cl_2 (oxidizing conditions, provided from $PtCl_2$) and HCl (reductive conditions, provided from NH_4Cl) as transport media yielded several phases as small (< 1 mm), often well-formed crystals: synth. rutile, synth. anatase, synth. corundum, synth. mullite, Sc_2O_3, and synth. thortveitite ($Sc_2Si_2O_7$), whereas experiments with $HgCl_2$ as transport medium yielded no crystals at all. Studies with $TeCl_4$ have not been performed yet. The growth of synthetic anatase confirms that metastable compounds can be prepared at high temperatures using this technique.

Chemical transport reactions have not been used so far to produce single crystals of mullite, but only to prepare very thin, microcrystalline protective mullite coatings on SiC ceramic bodies, e.g., [7-10]. Our studies show that mullite single crystals with dimensions suitable for determination of various physico-chemical properties can be prepared using the technique of chemical transport reactions.

The average crystal structures of two colourless, prismatic mullite crystals from different experiments (starting materials: Sc_2O_3 + Al_2O_3 + TiO_2 + SiO_2; transport medium: Cl_2 or HCl) were determined from highly redundant single-crystal X-ray diffraction data (Mo-Kα radiation, CCD area detector) and refined in space group *Pbam* to R1(F) values of 2.0 and 1.9 %, respectively. No first- or second-order satellite reflections or any streaking were recognisable on the recorded CCD frames, despite overexposure.

The two crystals have the following, similar unit-cell parameters (first value refers to crystal grown using Cl_2): a = 7.591(2) / 7.600(2), b = 7.709(2) / 7.700(2), c = 2.895(1) / 2.894(1) Å, and V = 169.41(9) / 169.36(9) $Å^3$. The structure of the Cl_2-grown crystal shows a reasonably good agreement with the mullite model (both coordinates and occupancies) proposed by SAALFELD & GUSE [11] or ANGEL & PREWITT [12], whereas the other, HCl-grown crystal has distinctly different occupancies, and appears to be poorer in Si. Largest variations in metal-oxygen bond lengths are shown by the T*-Oc* distances. The unit-cell dimensions of both crystals are anomalously enlarged (especially the b-axes), and can, at present, only be explained by incorporation of impurity cations (Ti and/or Sc?), but not by a simple variation of the Al:Si ratio, or by the additional influence of quenching the grown crystals. Results from chemical analyses are not available yet, but will ultimately provide a more detailed picture of these anomalous mullites.

Financial support by the Austrian Science Foundation (FWF) (Grant P15220-N06) is gratefully acknowledged.

References

[1] KOLITSCH, U. & TILLMANNS, E. (2003): Sc_2TiO_5, an entropy-stabilized pseudobrookite-type compound. - Acta Crystallographica, E59, i36-i39.

[2] KOLITSCH, U. & TILLMANNS, E. (2003): $Bi_3ScMo_2O_{12}$: the difference from $Bi_3FeMo_2O_{12}$. - Acta Crystallographica, E59, i43-i46.

[3] KOLITSCH, U. & TILLMANNS, E. (2003): $Li_3Sc(MoO_4)_3$: substitutional disorder on three (Li,Sc) sites. - Acta Crystallographica, E59, i55-i58.

[4] KOLITSCH, U. & TILLMANNS, E. (2003): The crystal structure of synthetic $Sc_2Si_2O_7$ at 100, 200 and 293 K: thermal expansion and behaviour of the Si_2O_7 group. - Zeitschrift für Kristallographie, Supplement No. 20, 139.

[5] KOLITSCH, U. & TILLMANNS, E. (2003): Synthesis and crystal structure of $K_2ScFSi_4O_{10}$, and its close relation to narsarsukite. (To be submitted).

[6] GRUEHN, R. & GLAUM, R. (2000): Neues zum chemischen Transport als Methode zur Präparation und thermochemischen Untersuchung von Festkörpern. - Angewandte Chemie, 112, 706-731. (in German).

[7] BASU, S. N. ET AL. (1998): Formation of mullite coatings on silicon-based ceramics by chemical vapor deposition. - International Journal of Refractory Metals & Hard Materials, 16, 343-352.

[8] ARMAS, B. ET AL. (2001): Low-pressure chemical vapor deposition of mullite layers using a cold-wall reactor. Surface and Coatings Technology, 141, 88-95.

[9] HOU, P. ET AL. (2001): Structure and high-temperature stability of compositionally graded CVD mullite coatings. - International Journal of Refractory Metals & Hard Materials, 19, 467-477.

[10] SOTIRCHOS, S. V. & NITODAS, S. F. (2002): Factors influencing the preparation of mullite coatings from metal chloride mixtures in CO_2 and H_2. - Journal of Crystal Growth, 234, 569-583.

[11] SAALFELD, H. & GUSE, W. (1981): Structure refinement of 3:2-mullite ($3Al_2O_3.2SiO_2$). - Neues Jahrbuch für Mineralogie, Monatshefte, 1981, 145-150.

[12] ANGEL, R. J. & PREWITT, C. T. (1986): Crystal structure of mullite: A re-examination of the average structure. - American Mineralogist, 71, 1476-1482.