

tetrahedrally and octahedrally coordinated aluminum atoms the same relative displacement (percentage movement in relation to the ionic radii) is observed which is twice as high as compared with the values calculated for the bismuth and oxygen atoms.

For $(\text{Bi}_{0.8}\text{Sr}_{0.2})_2\text{Al}_4\text{O}_9$, the thermal expansion parameter of $5.3 \cdot 10^{-6}$, $9.6 \cdot 10^{-6}$, $6.7 \cdot 10^{-6}$ and $2.3 \cdot 10^{-5}$ for the lattice parameters a , b , c , and V , respectively, measured during heating runs of two different samples, differ slightly from the corresponding parameters of the pure bismuth aluminate. Additionally, during the cooling run the thermal expansion for the c lattice parameter ($7.9 \cdot 10^{-6}$) differs at most from the heating measurement. But in both cases, the samples were heated above their stability temperature of 1070 – 1130 K and this parameter reflects the remaining $(\text{Bi}/\text{Sr})_2\text{Al}_4\text{O}_9$ phase to be nearly free of strontium which is confirmed by Rietveld refinements.

For $\text{Bi}_2\text{Fe}_4\text{O}_9$, a similar behavior as for the corresponding aluminate or gallate [3] is observed except the decomposition temperature, which is 1232 K for the ferrate.

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Keywords: mullite related phases; high temperature; powder diffraction

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Synthesis and Crystal Structure of $\text{Zr}_{0.43}\text{Gd}_{0.57}\text{O}_{1.07}\text{N}_{0.43}$. Eberhard Schweda^a, Stefanie Meyer^a. ^aUniversität Tübingen, Institut für Anorganische Chemie, Ob dem Himmelreich 7 D-72074 Tübingen.

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The nitridation of $\text{Zr}_{0.43}\text{Gd}_{0.57}\text{O}_{1.71}$ using gaseous ammonia leads to a solid solution type nitride oxide with the composition $\text{Zr}_{0.43}\text{Gd}_{0.57}\text{O}_{1.07}\text{N}_{0.43}$. The reaction path was recorded using in situ X-ray diffraction. The nitridation introduces additional vacancies into the fluorite lattice and the composition of the title compound counts for an M_2X_3 structure type if there is any ordering of vacancies. Unlike $\text{Zr}_{0.43}\text{Er}_{0.57}\text{O}_{1.07}\text{N}_{0.43}$, which crystallizes in Ia3 with a bixbyite type structure and ordered vacancies [1], the Gd compound has a complete statistical distribution and crystallizes in space group Fm3m with lattice constant $a = 527.2(2)$ pm

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Crystallization and Microstructure Evolution of TiO₂ Thin Films and Powders Studied by XRD Total Pattern Fitting and Stress Analysis. Radomir Kužel^a, Zdenek Matěj^a, Lea Nichtová^a. ^aDepartment

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Different TiO₂ samples – magnetron deposited amorphous and nanocrystalline thin films and powders – were annealed both off-situ and in-situ in XRD high-temperature chamber and their microstructure evolution with temperature and time was studied.

Coplanar XRD grazing incidence measurements (2θ scans) in parallel beam setup with a mirror were evaluated by both the profile fitting of peak clusters and total pattern fitting. Residual stresses were analyzed by sin²ψ method and X-ray reflectivity curves were studied as well. Because of severe peak overlap the whole pattern evaluation was applied in most cases. We have extended flexible modular system of Crystal Objects and Fox program [1] for studies of real structure of thin films. Applied model include the following features. Variable peak positions determined by variable lattice parameters and zero shift error, possibly also by residual stress. Peak intensities calculated by the ObjCryst library from a known crystal structure model. They can be modified by absorption and the texture correction obtained from the known model of ODF after numerical integration over all crystallites with diffracting (hkl) planes perpendicular to direction of the measured diffraction vector, or they can be varied independently. Peak profiles are given by numerical convolution of the known instrumental function described by the pseudo-Voigt function and physical profiles including several free parameters (models). The size broadening is described by the model of log-normal distribution of spherical crystallites or distribution given by a histogram like in [2], the strain broadening either by phenomenological microstrain or dislocation model. Stacking faults and twins can be included too. Individual layers in the system are characterized by their thickness and linear absorption coefficient.

It was shown that crystallization of very thin *amorphous* films (below about 300 nm) is rather slow. Fast crystallization occurred in the temperature range 220–300°C depending on the films thickness. In this case relatively large crystallites (> 100 nm) grew quickly from the very beginning of crystallization and they were not changed with increasing annealing time. The microstructure evolution was different for powders when the crystallites grew with annealing time to some saturated values determined by the annealing temperature. By contrast as-deposited *nanocrystalline* films (crystallite size ~ 5 nm) or nanocrystalline powders showed the fine microstructure stable to quite high temperatures (500 °C) before the strain relaxation and crystallite growth was observed.

During the crystallization of amorphous films tensile residual stresses were generated. They were of simple uniaxial character and strongly increase with decreasing film thickness.

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