

assume a minimum of melting point in the compositional range around $\text{Sm}_{0.6}\text{Ce}_{0.4}\text{PO}_4$. First results particularly related to crystal structure analysis of the investigated ceramics will be presented.

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Raman spectra of Synthetic Orthophosphates used for Nuclear Waste Management

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One of the central tasks in nuclear waste management is the safe conditioning of actinides like e.g. U, Th or Pu resulting from the re-processing of nuclear fuel. Besides borosilicate glasses promising candidates to accomplish that task safely are ceramic orthophosphates that own the crystal structure and properties of the mineral monazite. Monazite is monoclinic (SG $P2_1/n$) and exhibits an extraordinary chemical durability and radiation resistance [1,2,3]. For the development of new conditioning matrices orthophosphates with compositions LnPO_4 (Ln = La, Ce, Nd, Sm, Eu) were synthesized as first simulation phases without incorporated actinides. These phases were partly radiated by the bombardment with heavy Kr-ions in order to simulate radiation damage caused by α -emitters (α -recoil effect).

The quality of all phases (radiated and non-radiated) was first characterized by powder x-ray diffraction. The short range order and medium range order was investigated by raman spectroscopy. Using this technique structural changes due to radiation damage can be detected quite easily [4,5,6]. Resulting raman spectra show a high resolution and allow the discrimination of up to 30 different raman frequencies.

As a first result significant correlations between chemical composition, crystal structure, radiation damage and thermodynamic properties of the investigated ceramics can be detected and will be demonstrated in detail.

The findings of our investigation will be the basis for the further development and evaluation of *real* monazite-type conditioning ceramics containing larger amounts of the actinides U, Th, Pu, Am, Cm and Np.

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XRD analysis of the corrosion products of research reactor fuel elements

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Corrosion experiments of unirradiated $\text{UAl}_x\text{-Al}$ and $\text{U}_3\text{Si}_2\text{-Al}$ research reactor fuel elements were carried out under repository relevant conditions in order to identify and quantify the secondary phases formed by reactions with formation waters being expected in final repositories due to an accidental influx from the enclosing salt formations. This analysis is important for safety assessment issues as such phases quantitatively may act as a barrier against the migration of the released radioactive inventory. In detail the anaerobic experiments were carried out in glass autoclaves at 90°C in repository relevant solutions of defined composition [1]. After termination of the corrosion period WAXS measurements and Rietveld analysis were the major methods being applied for the identification and quantification of the crystalline and amorphous corrosion products which have been subdivided into different grain size fractions previously.

The corrosion products, i. e. the secondary phases of the research reactor fuel elements were identified via "Search/Match" database retrieving. The identified phases were LDH structures, lesukite (aluminium chlorohydrate), elemental iron, residues of uncorroded nuclear fuel, and different iron containing phases like akaganeite, goethite, and lepidocrocite. The quantitative analysis showed that LDH compounds and lesukite are the major crystalline phases which are observed. Rietveld analysis also revealed the content of amorphous phases. To account for an accurate determination of the phase quantities, i. e. for the application of the Brindley [2] correction the average particle diameter has previously determined by REM and image analysis.

For safety assessments the potential for retention of radionuclides has to be focused on the sorption capacities of the major phases as these may additionally applied as a backfilled barrier in order to prevent the migration of radionuclides out of the final repository in deep geological formations.

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Stability and Conductivity of Ce-doped Pyrochlores for SOFCs applications

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Solid Oxide Fuel Cells (SOFCs) are highly efficient and environmentally friendly energy conversion devices with a large variety of potential applications. A SOFC has 3 main components: the cathode, which has to have high electronic/ionic conductivity, to be chemically compatible with other cell components, stable in oxidizing atmospheres and a thermal expansion coefficient similar to other components; the electrolyte that should be ionically conductive, electronically insulating, chemically stable at high temperatures and in reducing and oxidizing environments, free of porosity and with thermal expansion that matches electrodes and finally, the anode which should be electrically conductive, stable in reducing atmosphere and should have high electrocatalytic activity, similar thermal expansion

coefficient to those of the closer components and be chemically compatible with them.

SOFCS operate at high temperatures under either oxidising or reducing atmospheres over a long period of time. This can create different problems such as interface reactions which could promote the formation of insulating phases, limiting their long-term stability [1]. In light of this, the idea is to find new materials that are very stable at high temperatures and have the properties described above.

Here we report the investigation of the family of pyrochlores of general formula $A_2B_2O_7$ (where A is a trivalent ion, usually a rare earth, and B is a tetravalent ion) which are known to exhibit oxygen ion conductivities of the order of 10-2 S/cm at 1000 °C, making them promising candidates as electrolytes. Examples include: $Gd_2(Zr_{1-x}Sn_x)_2O_7$, [2], Ca-doped $Gd_2Ti_2O_7$ [3] and Ca-doped $Gd_2(Zr_{0.3}Ti_{0.7})_2O_7$ [4].

In particular we have focused on $Ln_2Zr_2O_7$ (Ln= Lanthanide) whose structure is mainly governed by the ion size difference between Ln^{3+} and Zr^{4+} [5]. These materials have the properties needed to be a good electrolyte (high melting point, high thermal expansion coefficient, low thermal conductivity, high thermal stability and high electrical conductivity) in SOFCs [6]. Among the rare earth zirconates, $Ce_2Zr_2O_7$ bears additional interest due to the catalytic application of the CeO_2 - ZrO_2 in several chemical processes in industry and automobiles [7].

We have study the stability in air of the solid solutions $La_{2-x}Ce_xZr_2O_7$ and $Gd_{2-x}Ce_xZr_2O_7$ and the effect of the Ce- doping on the conductivity. The X-ray diffraction studies show, that the La- series keeps the pyrochlore structure up to $x = 0.5$, while the Gd one adopts the fluorite structure. These results will be correlated to the conductive behavior of these materials.

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Crystal Structure and Diffusion Path of Mixed Conductors $PrBa_{1-x}Sr_xCo_2O_{5+}$ ($x = 0$ and 0.5)

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Mixed oxide-ionic and electronic conducting ceramics (MIECs) will become increasingly important for future environmentally friendly ("green") societies, because the MIECs are used as materials for oxygen separation membranes and cathodes of solid-oxide fuel cells (SOFCs). Oxygen is an important reactant in the industrial chemical processes and air is usually utilized as the oxygen source due to the cost problem. For lower temperature devices, novel MIECs with higher oxide-ion diffusivity are required. For this purpose, it is of vital importance to investigate the oxide-ion diffusion mechanism at an atomic scale. Recently, layered perovskite oxides such as $PrBaCo_2O_{5+}$, with cation order has been reported for cathode applications in the next generation of

intermediate temperature SOFCs operations [1]. $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ exhibits better cell performance [2]. Parfitt *et al.* suggested that cation order gives larger oxide-ion diffusivity and larger activation energy by molecular dynamics [3]. However, the structural origin, cation disorder and oxygen diffusion mechanism in $PrBa_{1-x}Sr_xCo_2O_{5+}$ is unclear.

In the present work, the crystal structures of $PrBaCo_2O_{5+}$ and $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ have been studied through neutron powder diffractometry at 1000 °C. The $PrBaCo_2O_{5+}$ and $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ were identified to be tetragonal $P4/mmm$ and $Pm\bar{3}m$, respectively. The diffraction data were analyzed by a combination of the Rietveld analysis, maximum-entropy method (MEM) and MEM-based pattern fitting (MPF). The refined interstitial oxygen concentration δ in $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ is larger than that in $PrBaCo_2O_{5+}$. The refined oxygen atomic displacement parameters of $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ are larger than those in $PrBaCo_2O_{5+}$. The oxygen atom exhibited a large anisotropic thermal motions perpendicular to the Co-O bond, $U_{22}(O)$ ($=U_{33}(O)$) $>$ $U_{11}(O)$. MEM nuclear-density distributions also indicated large anisotropic thermal motions of oxygen atoms perpendicular to the Co-O bond [4]. In the MEM nuclear density distributions, the oxygen diffusion paths in both of $PrBaCo_2O_{5+}$ and $PrBa_{0.5}Sr_{0.5}Co_2O_{5+}$ were visualized.[5]

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In-situ high temperature powder diffraction study of T/P91 steel oxidation

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Low chromium ferritic steels have been extensively studied for applications in power generating plant life time. Formation of dense, thick, and adherent chromia (Cr_2O_3) layer on stainless steel, which is considered like a good way to increase the oxidation resistance, is closely related to many parameters such as chromium content, temperature, oxidizing atmosphere, cycles frequency and time of exposure [1-3]. For grades with 9%Cr such as T/P91, the chromium content is not enough to fulfil the protective action by creating a continuous chromia scale over 600°C. As a consequence, iron oxidation can occur, and lead to the total destruction of the material [2]. Corrosion mechanisms were proposed after several studies of post-mortem samples but no clear interpretation was found about oxide formation process before critic behaviour of the steel ("break away").

The key to a successful development of T/P91 steel grade lies in a better understanding of the material reactivity at high temperature through the observation and characterization of the germination and growth of the surface oxide layers occurring within the first oxidation instants. Three oxides can mainly be formed under oxidation conditions: Cr_2O_3 , Fe_2O_3 and Fe_3O_4 . If the first one has a protective action against corrosion, the appearance and growth of the other two oxides can lead to the catastrophic behaviour.

In order to better understand the oxidation mechanisms of T/P91 steel, an in-situ diffraction experiment was performed at the ID31 High