Crystal structure and thermal expansion of the La$_{1-x}$Ca$_x$TiO$_3$ and La$_{2(1-x)/3}$Ca$_x$TiO$_3$ solid solutions

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One possible candidate as anode material for SOFC could be lanthanum doped calcium titanate, because it was found that increasing Ti/Cr ratios in La$_{1-x}$Ca$_x$Cr$_{1-y}$Ti$_y$O$_{3-\delta}$ are accompanied by corresponding increases of the electrical conductivity at reducing conditions [1]. Recently, high electrical conductivity and acceptable catalytic activity in SOFC anode conditions were found for analogous series La$_{1-x}$Sr$_x$TiO$_{3-\delta}$ [2]. In this work two different series of perovskite-type compounds La$_{1-x}$Ca$_x$TiO$_3$ (x = 0 - 1.0) and La$_{2(1-x)/3}$Ca$_x$TiO$_3$ (x = 0, 0.1, 0.4 and 0.8) were prepared, their crystal structures and thermal expansion as functions of calcium content were investigated. The crystal structures were investigated by means of the powder diffraction technique using a Siemens D5000 powder X-Ray diffractometer Structure refinement was performed by using full-profile Rietveld method. All calculations were performed using the WinCSD (Crystal Structure Determination) program package. High-resolution powder diffraction technique and synchrotron radiation with $\lambda = 0.70787$ Å were used for the determination of thermal expansion in the temperature range 293 to 1273 K in air. The diffraction experiments were carried out at beamline B2 by a powder diffractometer equipped with STOE furnace and a newly developed IP-detector.

The crystal structures of the La$_{1-x}$Ca$_x$TiO$_3$ compounds were characterised at room temperature as orthorhombic in space group $Pbnm$ (samples with 0.7 ≤ x ≤ 1) and as rhombohedral in space group $R\bar{3}c$ (x = 0.6 sample). Lattice parameters and some interatomic distances of La$_{1-x}$Ca$_x$TiO$_3$ as functions of Ca content are presented in Fig. 1.

![Fig. 1. Lattice parameters and R-O interatomic distances in La$_{1-x}$Ca$_x$TiO$_3$ structures](image)

At room temperature three different perovskite-like structures has been found for A-cation deficient La$_{2(1-x)/3}$Ca$_x$TiO$_3$ compounds: orthorhombic $Pbnm$ structure for the composition with x = 0.8, orthorhombic $Imma$ structure for x = 0.4, and monoclinic $P2/m$ (or possibly orthorhombic $Cm2m$) structure for x = 0.1. La$_{0.4}$Ca$_{0.4}$TiO$_3$ undergo two phase transitions in the temperature range 300 – 1200 K: $Imma – I4/mcm$ at 480 K and $I4/mcm – Pm3m$ at 1150 K (Fig. 2). Monoclinic-to-tetragonal
phase transition is detected for La$_{0.6}$Ca$_{0.1}$TiO$_3$ at 770 K. Thermal expansions of La$_{0.4}$Ca$_{0.6}$TiO$_3$ in $a$- and $c$-directions are practically the same up to ~900 K (Fig. 2). A slope change of the $a$-parameter is observed at temperatures higher than 900 K. Changes of the slope of the $a$-parameter and cell volume correspond to the observed anomalies of the thermal expansion coefficient, obtained by dilatometric method (Fig. 3).

Fig. 3 represents the linear thermal expansion of the La$_{0.4}$Ca$_{0.6}$TiO$_{3.8}$ ceramic sample measured in air by dilatometry and XRD in comparison with YSZ ceramics. La$_{0.6}$Ca$_{0.1}$TiO$_3$ shows near linear expansion in the whole temperature range investigated. The thermal expansions of La$_{0.4}$Ca$_{0.4}$TiO$_{3.8}$ and YSZ samples measured by dilatometric method coincide almost fully.

Fig. 2. Temperature dependencies of the lattice parameters and interatomic distances in La$_{0.4}$Ca$_{0.4}$TiO$_3$.

Fig. 3. Thermal expansion of the La$_{0.4}$Ca$_{0.4}$TiO$_{3.8}$ ceramic sample measured in air by dilatometry and XRD in comparison with YSZ ceramics.

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References
