# SYNTHESIS AND CHARACTERIZATON OF THE RARE-EARTH ZIRCONATE PYROCHLORE $RE_2Zr_2O_7$ AND THE $\kappa$-$RE_2Zr_2O_8$ PHASES (RE=La, Y, Gd, Pr, Ce and Zr)


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## INTRODUCTION

**Rare-earth metals are commonly used in the formation of zirconates in the form of solid solutions. Mixed Ce-Zr oxides and compounds based on its structure, supply oxygen for the oxidation processes and store oxygen under lean reaction conditions. Tetragonal solid solutions *t*-$Ce_{0.5}Zr_{0.5}O_2$ and *t*-$La_{0.1}Y_{0.1}Gd_{0.1}Pr_{0.1}Ce_{0.1}Zr_{0.5}O_2$ were synthesized using a low-cost and environmentally friendly citrate sol-gel route followed by calcination at 600 °C. Solid solutions were reduced by calcination at 1500 °C in a gaseous mixture of 3% hydrogen in argon, to form pyrochlore phases $Ce_2Zr_2O_7$ and $(La_{0.2}Y_{0.2}Gd_{0.2}Pr_{0.2}Ce_{0.2})_2Zr_2O_7$. The last step of phase transformations is the re-oxidation of pyrochlore phases at 600 °C to kappa phases, $\kappa$-$Ce_2Zr_2O_8$ and $\kappa$-$(La_{0.2}Y_{0.2}Gd_{0.2}Pr_{0.2}Ce_{0.2})_2Zr_2O_8$, respectively. Structural differences between tetragonal, pyrochlore and kappa forms of synthesized compounds were observed. The reversible exchange of $Ce^{4+}$ to $Ce^{3+}$ and vice versa makes ceria-based materials suitable as catalysts in oxidation reactions. [1,2]**

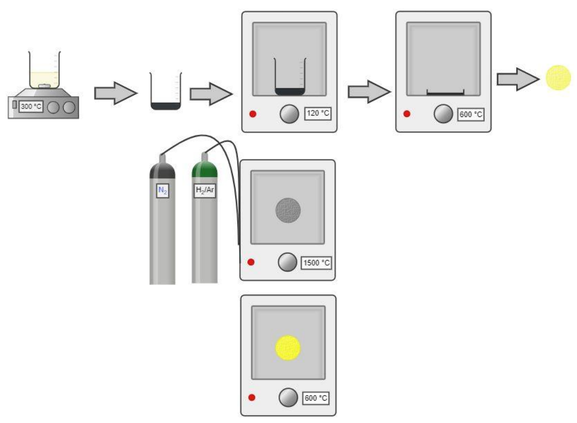


**Figure 1. Step-by-step route for the synthesis of different rare-earth zirconate phases**

## METHODS

**The sol-gel method using citric acid as a precursor and nitrate salts of rare earth metals was chosen for the preparation of the initial compounds *t*-$Ce_{0.5}Zr_{0.5}O_2$ and *t*-$La_{0.1}Y_{0.1}Gd_{0.1}Pr_{0.1}Ce_{0.1}Zr_{0.5}O_2$. Inorganic salts were dissolved in 10 % citric acid and $NH_3$ (conc.) was added to obtain pH=5 solution. Mixture was heated at 300 °C and well stirred until only a black mass remained. The obtained mass was crushed in a mortar and subjected to the calcination process in a muffle furnace at 600 °C for 8 hours (Figure 1.).**

**A Carbolate Gero Tube Furnace was used to reduce the obtained compounds to the pyrochlore phases $Ce_2Zr_2O_7$ and $(La_{0.2}Y_{0.2}Gd_{0.2}Pr_{0.2}Ce_{0.2})_2Zr_2O_7$, under nitrogen flow and 3% hydrogen in argon atmosphere, respectively.**

**$\kappa$-phases, $\kappa$-$Ce_2Zr_2O_8$ and $\kappa$-$(La_{0.2}Y_{0.2}Gd_{0.2}Pr_{0.2}Ce_{0.2})_2Zr_2O_8$, were obtained by calcination process in a muffle furnace at 600 °C for 4 hours.**

**Table 1. Rietveld analysis of *pyr*-$Ce_2Zr_2O_7$ and $\kappa$-$Ce_2Zr_2O_8$ XRD**

| Compound | *pyr*-$Ce_2Zr_2O_7$ | $\kappa$-$Ce_2Zr_2O_8$ |
|---|---|---|
| Crystal system | Cubic | |
| Space group | Fd–3m | $P2_13$ |
| a (Å) | 10.73 | 10.56 |
| V (Å$^3$) | 1236.17 | 1178.38 |
| Z | 8 | 1 |
| $R_p$, $R_{wp}$, $R_e$ | 27.0, 21.7, 8.52 | 19.5, 14.3, 5.93 |
| $\chi^2$ | 6.5 | 5.8 |
| Calculated density (g/cm$^3$) | 6.176 | 6.659 |
| Phase composition (wt.%) | 100 | |
| Average crystallite size (nm) | 33.12 | 82.58 |
| Average microstrain (×10$^{-4}$) | 8.79 | 4.23 |

**Table 2. Rietveld analysis of *pyr*-LYPGCZ$r_2O_7$ and $\kappa$-LYPGCZ$r_2O_8$ XRD**

| Compound | *pyr*-LYPGCZ$r_2O_7$ | $\kappa$-LYPGCZ$r_2O_8$ |
|---|---|---|
| Crystal system | Cubic | |
| Space group | Fd–3m | $P2_13$ |
| a (Å) | 10.6673 | 10.6173 |
| V (Å$^3$) | 1213.86 | 1196.87 |
| Z | 8 | 1 |
| $R_p$, $R_{wp}$, $R_e$ | 28.0 22.0 5.94 | 24.9 17.7 6.12 |
| $\chi^2$ | 13.67 | 8.376 |
| Calculated density (g/cm$^3$) | 6.289 | 6.556 |
| Phase composition (wt.%) | 100 | |
| Average crystallite size (nm) | 38.66 | 62.33 |
| Average microstrain (×10$^{-4}$) | 4.47 | 4.23 |

## RESULTS

**All synthesized materials were characterized by the Rietveld refinement of X-ray powder diffraction patterns (Table 1. and Table 2.).**

**X-ray powder diffraction patterns show that *t*-$Ce_{0.5}Zr_{0.5}O_2$ and *t*-$La_{0.1}Y_{0.1}Gd_{0.1}Pr_{0.1}Ce_{0.1}Zr_{0.5}O_2$ contain tetragonal structure since pyrochlore and $\kappa$- phases crystallize in cubic crystal system but in different spacegroups (Figure 2.).**

**Raman spectroscopy was used to complement XRD analysis and to calculate the $Ce^{3+}$/ $Ce^{4+}$ ratio (Figure 3.).**

**Scanning electron microscopy coupled with Energy-dispersive X-ray spectroscopy (SEM-EDS) was a useful method to inspect the morphology and chemical content of each compound (Figure 4.).**

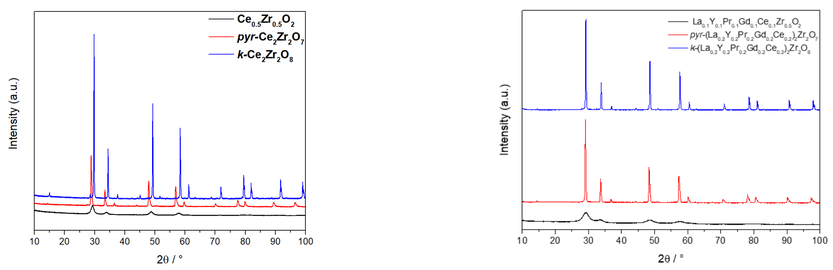


**Figure 2. XRD patterns of synthesized rare-earth different phases zirconates**

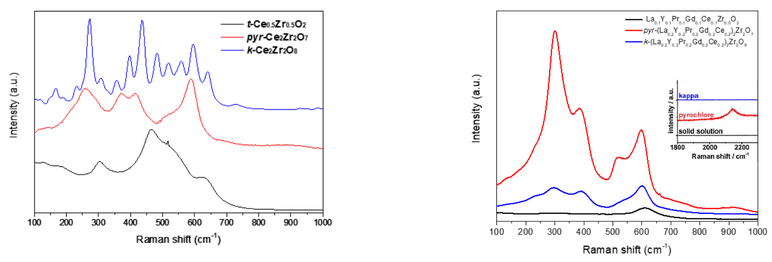


**Figure 3. Raman spectrums of synthesized rare-earth different phases zirconates**

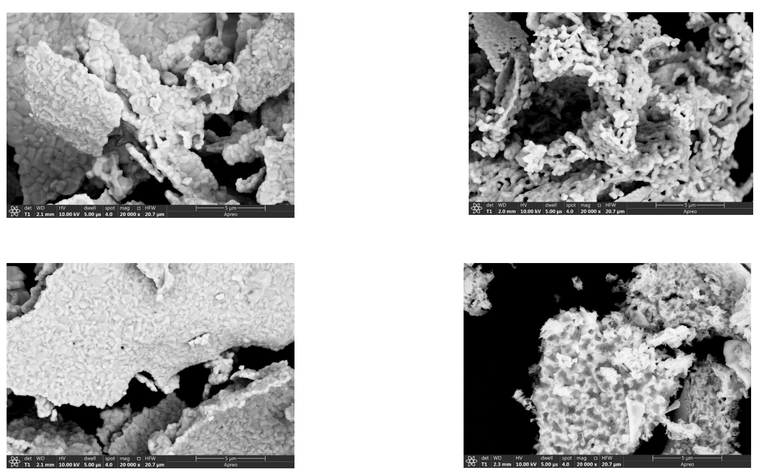

**Figure 4. SEM images of Ce-Zr based pyrochlore and kappa phase (left) and La, Y, Pr, Gd, Ce, Zr based (right)**

## CONCLUSIONS

**Rietveld analysis of XRD patterns showed that synthesized zirconates crystallize in tetragonal and cubic crystal systems in different space groups.**

**Using Raman spectroscopy, it was proven that $Ce^{3+}$ ions are contained in the pyrochlore phase, which is manifested by the strength of the signal at 2100 $cm^{-1}$. The reversible exchange of $Ce^{4+}$ to $Ce^{3+}$ and vice versa makes ceria-based materials suitable as catalysts in oxidation reactions.**

## REFERENCES


[1] S. Urban et al., *Appl. Catal. B-Environ.* **197** (2016) 23-34.

[2] S. Urban et al., *Chem. Mater.* **29** (2017) 9218-9226.