

# Dielectric properties of CaZrO<sub>3</sub> investigated by THz-TDS.

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**Abstract**—CaZrO<sub>3</sub> doped samples were prepared by using the solution combustion method. The higher powder sintering temperature induced slightly higher crystallinity in the studied samples with higher refractive indexes found. The differences in the dielectric behaviour and electronic conductivity of the samples may be attributed to the improved crystals order. However, a more detailed investigation of these materials is required.

## I. INTRODUCTION

CALCIUM zirconates (CaZrO<sub>3</sub>) are known for their interesting optical, electrical, and physico-chemical properties. The electronic, electro-mechanical, and conductive properties of CaZrO<sub>3</sub> doped with specific trivalent rare earth ions promote optical upconversion processes, where the absorption of two or more lower-energy photons leads to the emission of a higher energy photon. The upconversion materials are based on the f-f transitions of rare earth dopants, which show rich luminescence spectra consisting of a large number of distinct transition lines. Thus upconverting phosphor materials based on CaZrO<sub>3</sub> can be synthesized which are suitable for diode lasers, display devices, and other photonic applications with excitation in the near infrared (NIR) region.[1,2] Only a few reports dedicated to dielectric or spectral properties of CaZrO<sub>3</sub> in the far infrared region can be found in the literature.

## II. MATERIALS AND METHODS

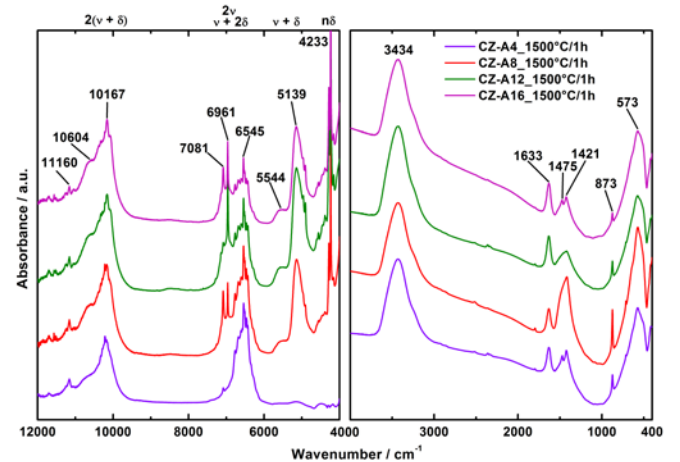
For the synthesis of CaZrO<sub>3</sub> the Pechini method was used, which involves chelation of water dissolved salts by citric acid and esterification by ethylene glycol. The resulting gel was first calcined in air at 600°C for 1h; then ground and pressed into discs of about 7 mm diameter and 1 mm thickness. Prepared discs were fired at 1300 and 1500°C for 1h and used for terahertz time domain spectroscopy (THz-TDS) measurements. Part of the fired material was ground in an agate mortar and used for X-ray diffraction measurements (XRD) and Fourier transform infrared (FTIR) spectroscopy in mid-IR and NIR region.[3] The chemical compositions of the samples resulting from component mixing during the synthesis are summarised in Table 1.

Sample	Chemical composition
CZ-A4	Er <sub>0.05</sub> Yb <sub>0.02</sub> CaZrO <sub>3</sub>
CZ-A8	Er <sub>0.02</sub> Yb <sub>0.02</sub> CaZrO <sub>3</sub>
CZ-A12	Er <sub>0.01</sub> Yb <sub>0.02</sub> CaZrO <sub>3</sub>
CZ-A16	Er <sub>0.005</sub> Yb <sub>0.02</sub> CaZrO <sub>3</sub>

**Table 1.** Chemical compositions of synthesised CaZrO<sub>3</sub>:Er<sup>3+</sup>, Yb<sup>3+</sup> powders.

## III. RESULTS

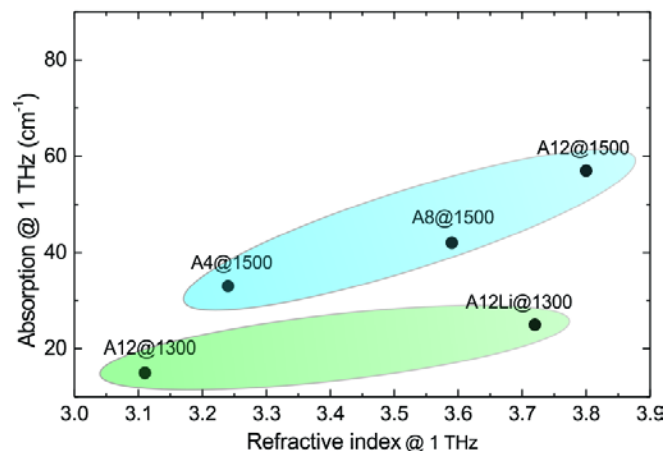
The mid-IR and NIR spectra of synthesized CaZrO<sub>3</sub> fired at 1500°C are shown in Figure 1. In the mid-IR region there are pronounced absorption bands of the water stretching vibration ( $\nu$ ) at 3434 cm<sup>-1</sup> and deformation vibration ( $\delta$ ) at 1633 cm<sup>-1</sup>, indicating that the fired samples adsorbed some water molecules from the air. The structural vibrations of CaZrO<sub>3</sub> can be seen as Zr–O stretching vibrations located at around 1420-1480 cm<sup>-1</sup> and deformation vibrations at 573 and 873 cm<sup>-1</sup>. The combinations of these absorption bands are also seen in the NIR spectrum. Corresponding combinations of stretching  $\nu$  and bending  $\delta$  bands are indicated above the graph, where linear and multiple combinations such as  $n\delta$  at 4233 cm<sup>-1</sup>,  $(\nu+\delta)$  around 5139 cm<sup>-1</sup> ( $\nu+n\delta$ ) at 6545-7081 cm<sup>-1</sup> or  $n(\nu+\delta)$  around 10167-11160 cm<sup>-1</sup> are typically observed (Figure 1).



**Figure 1.** Mid-IR (right) and NIR (left) spectra of synthesized CaZrO<sub>3</sub> fired at 1500°C.

The preliminary results obtained by THz-TDS in transmission mode in the frequency range of about 0.2-3.0 THz are shown in Figure 2. The material absorption as a function of the refractive index almost doubled when the Er<sup>3+</sup> content in the material decreased from 5 to 1 mol % (A4 ~ 5 mol %, A8~ 2 mol %, A12~ 1 mol %), while the refractive index (RI) increased from 3.25 to 3.80. This behaviour is strongly affected by sintering temperature as the sample A12 sintered at 1300°C showed more than 5 times lower absorption and the RI of 3.11. The addition of Li<sup>+</sup> ions to the structure increased both absorption and the RI to 3.72. The X-ray diffraction patterns proved the structural similarity of perovskite materials sintered at different temperatures; however, the higher temperature induced slightly higher crystallinity in the studied samples. The differences in their

dielectric behaviour and electronic conductivity may therefore be attributed to the improved crystals order, but better understanding of these systems requires a more detailed investigation.



**Figure 2.** Effect of  $\text{Er}^{3+}$  and  $\text{Li}^{+}$  content on  $\text{Yb}^{3+}$  doped  $\text{CaZrO}_3$  absorption properties as function of refractive index of the materials sintered at 1300 and 1500 °C.

#### IV. SUMMARY

$\text{CaZrO}_3$  samples doped with rare earth elements  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ , and alkali metal  $\text{Li}^{+}$  were prepared by using the solution combustion method. XRD and FTIR confirmed the successful synthesis of perovskite structure. The higher powder sintering

temperature induced slightly higher crystallinity in the studied samples with higher refractive indexes found. The differences in the chemical compositions of the samples were reflected in their dielectric behavior. Electronic conductivity of synthesized compounds may be attributed to the improved crystal order. However, due to the lack of data in the literature, a more detailed investigation of these materials is required.

#### ACKNOWLEDGEMENT

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