Experimental report

12/01/2024

Proposal: DIR-300 **Council:** 4/2023

Title: Structural stability and structureevolution of Er2(Ti,Zr)2O7 and Lu2(Ti,Zr)2O7 oxides

Research area: Physics

This proposal is a new proposal

Main proposer: Milan KLICPERA

Experimental team: Milan KLICPERA
Filip HAJEK

Local contacts: Ines PUENTE ORENCH

Samples: A2(Ti,Zr)2O7

Instrument	Requested days	Allocated days	From	To
D1B	3	3	10/11/2023	13/11/2023

Abstract:

The rare-earth oxides of the general formula A2B2O7 are of great interest to the condensed matter community for their application potential. Significant effort has been dedicated to finding materials with improved thermomechanical properties and higher ionic conductivity, both tightly related to details of their crystal structure. The present experiment is directed at the evolution of the crystal structure in two series of solid solutions from the A2B2O7 family, thoroughly investigated by our recent neutron diffraction and X-ray and neutron pair distribution function, through a set of structural transitions at high temperature. We expect thermally activated structural changes, that is, temperature-induced disorder on the oxygen anion (as well as cation) sites, which can be effectively studied by neutron diffraction. The proposed experiment on the D1B diffractometer is to reveal the details of structure of these application important materials.

Experimental report

Experimental title: Structural stability and structureevolution of $Er_2(Ti,Zr)_2O_7$ and $Lu_2(Ti,Zr)_2O_7$ oxides

Proposal number: **DIR-300**

Instrument: **D1B**

Date of experiment: 10. – 13.11. 2023

Local contact: Inés Puente Orench

Experimental team: Milan Klicpera, Filip Hájek

Affiliation: Charles University in Prague, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic.

Abstract:
The rare-earth oxides of the general formula $A_2B_2O_7$ are of great interest to the condensed matter community for their application potential. Significant effort has been dedicated to finding materials with improved thermomechanical properties and higher ionic conductivity, both tightly related to details of their crystal structure. The present experiment is directed at the evolution of the crystal structure in two series of solid solutions from the $A_2B_2O_7$ family, thoroughly investigated by our recent neutron diffraction and X-ray and neutron pair distribution function, through a set of structural transitions at high temperature. We expect thermally activated structural changes, that is, temperature-induced disorder on the oxygen anion (as well as cation) sites, which can be effectively studied by neutron diffraction. The proposed experiment on the D1B diffractometer is to reveal the details of structure of these application important materials.

Experiment and results:
For structure determination of selected $Er_2(Ti,Zr)_2O_7$ members and its evolution with temperature, the diffraction pattern were collected employing the **D1B** diffractometer and the **04TL20AN50 furnace** (reaching a temperature 1600 °C). We collected the diffraction patterns first at room temperature. Subsequently, the temperature was increased up to the maximum value allowed by the furnace, while the diffraction patterns were continuously measured. The diffraction patterns were collected typically in 5-min intervals, while the sample was heated with the rate of 1-1.5 °C/min. In addition, the measurement during the fast-cooling of the sample back to room temperature was done. Intermediate-statistics diffraction patterns were compared with each other and reasonably convoluted to maximise the output of the measurement. The diffraction patterns contained the contribution of Nb from the sample holder (*I m -3 m*, a = 3.3 Å) and evolution of its diffraction patterns with temperature.
Due to furnace operation requirements, we investigated three samples during three experimental days. Investigation of crystal structures and their development of the $Er_2Ti_{1.4}Zr_{0.6}O_7$, $Er_2Ti_{1.0}Zr_{1.0}O_7$ and $Er_2Ti_{0.4}Zr_{1.6}O_7$ compounds allowed us to map structural properties and stability within the $Er_2(Ti,Zr)_2O_7$ series. First member crystallises in a structure, which was believed to be of pyrochlore-type. However, additional intensity in several reflections evidence that the initial determination of the structure is not valid. We currently work on refinement of the diffraction data and identifying the crystal structure of this member. The second member is on the border between structures, resembling a more pyrochlore-like structure. The third member adopts the defect-fluorite structure, although diffuse scattering signal is clearly observed on top of the background.
The temperature evolution of the diffraction patterns reveals only subtle changes in the intensities of the diffraction peaks in all of the investigated compounds. No clear signs of additional peaks are observed in the

data, when comparing room temperature and 1600 ° C datasets. See the contour map in Fig. 1 as an example. The measured data reveal a standard thermal expanstion of the lattice. The investigated compounds adop stable structures up to high temperature, although the maximum temperature reached is significantly lower (by at least 600 °C) than melting temperature of these materials.

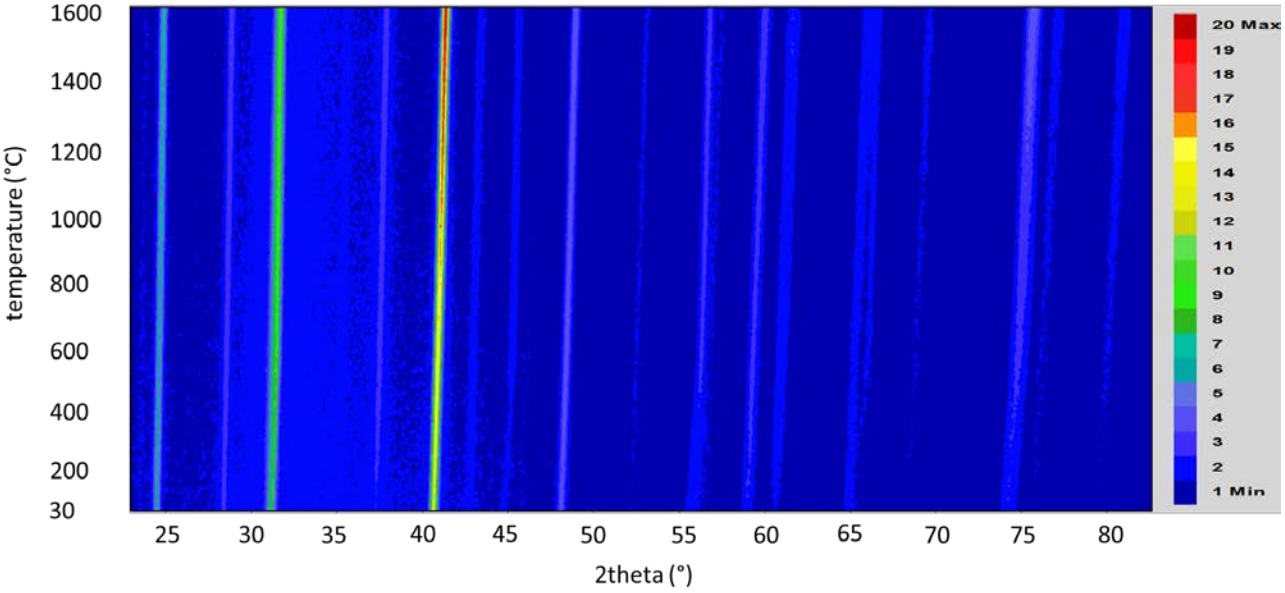

Fig.1 - Contour map of the the temperature evolution of the diffraction patterns of $Er_2Ti_{1.0}Zr_{1.0}O_7$ compound. No clear changes of intensity or additional peaks appearing at high temperature are observed.