

# High-temperature thermoelectric properties of $\text{Sr}_2\text{RuYO}_6$ and $\text{Sr}_2\text{RuErO}_6$ double perovskites influenced by structure and microstructure

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## Abstract

The high-temperature thermoelectric properties of  $\text{Sr}_2\text{RuYO}_6$  and  $\text{Sr}_2\text{RuErO}_6$  double perovskites were evaluated and reported for the first time. These compounds show high Seebeck coefficients not only at room temperature, but also at high temperature (for  $\text{Sr}_2\text{RuYO}_6$ ,  $S_{\text{RT}} \approx -475 \mu\text{V K}^{-1}$  and  $S_{1200\text{K}} \approx -250 \mu\text{V K}^{-1}$ ;  $\text{Sr}_2\text{RuErO}_6$ ,  $S_{\text{RT}} \approx -400 \mu\text{V K}^{-1}$  and  $S_{1200\text{K}} \approx -250 \mu\text{V K}^{-1}$ ). The  $n$ -type semiconducting behaviour dominates the resistivity values. Both compounds crystallize in a monoclinic unit cell (space group  $P2_1/n$ ). The lattice parameters are  $a = 5.7761(2)$ ,  $b = 5.7804(1)$ ,  $c = 8.1689(1)$ ,  $\alpha = \gamma = 90^\circ$  and  $\beta = 90.2087(8)^\circ$  for the  $\text{Sr}_2\text{RuYO}_6$ , and  $a = 5.7760(1)$ ,  $b = 5.7722(0)$ ,  $c = 8.1544(4)$ ,  $\alpha = \gamma = 90^\circ$  and  $\beta = 90.2099(7)^\circ$  for  $\text{Sr}_2\text{RuErO}_6$ . The unit cell can be described approximately as  $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ , where  $a_p$  is the unit cell parameter of the ideal cubic perovskite structure. High-resolution transmission electron microscopy shows an interesting three-dimensional micro-twin-domain texture where the  $c$  axis is placed in the three space directions. Structural transitions at high temperatures ( $T_1(\text{Sr}_2\text{RuYO}_6) \approx 920 \text{ K}$  and  $T_1(\text{Sr}_2\text{RuErO}_6) \approx 890 \text{ K}$ ) are observed by specific heat measurement in both compounds, which are found to have a strong influence on the Seebeck coefficient and electrical conductivity.

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## 1. Introduction

Compounds of the general formula  $\text{A}_2\text{BB}'\text{O}_6$  tend to adopt the perovskite structure when A is a large cation capable of 12-fold coordination by oxygen, while B and B' represent smaller cations suitable for octahedral coordination. A large difference in charge or size between B' and B can lead to an ordered arrangement in the perovskite-type lattice. Numerous compounds with this  $\text{A}_2\text{BB}'\text{O}_6$  stoichiometry have been synthesized and recently studied [1,2] and, for some, their magnetic, optical and transport prop-

erties have been reported. This study is focused on the double perovskite oxides  $\text{Sr}_2\text{BRuO}_6$ , where  $\text{B} = \text{Er}^{3+}$  and  $\text{Y}^{3+}$ . They are known to be antiferromagnetic insulators with a weak ferromagnetic component caused by a small canting of the  $\text{Ru}^{5+}$  and  $\text{B}^{3+}$  moments [3,4]. Recently, studies on double perovskite compounds with Co and Ru [5] and on strontium ruthenates [6] have also been proposed as potential thermoelectric materials because of their high electrical conductivity and Seebeck coefficient.

The absolute thermopower  $|S|$  is known to depend on the electronic structure of the materials and is insensitive to grain boundaries. In turn, small modifications of the unit cell parameters and the lattice distortion strongly influence  $S$  and the electrical resistivity  $\rho$ . For this reason,

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a carefully structural and microstructural characterization should be done in order to evaluate these effects on Seebeck coefficient  $S$  and resistivity  $\rho$ .

In this work, the crystal structures are studied by neutron powder diffraction, X-ray diffraction and transmission electron microscopy (TEM), while the transport properties are studied by Seebeck measurements, electrical ( $\sigma$ ) and thermal ( $\kappa$ ) conductivities. The valence state of Ru is studied by X-ray absorption (XANES).

The compositional and chemical stability of the samples plays an important role, especially in the evaluation of the properties at high temperatures. Thermogravimetric analyses combined with differential scanning calorimetry (DSC) are used to check possible instabilities of the systems. For example, any variation in the anionic composition may change the valence state of Ru and, consequently, the electronic properties of the compounds. As shown in the following, the evaluation of  $C_p$  as a function of temperature is also a good tool for monitoring possible structural transitions which can affect the transport properties. Finally, the relations between structure, microstructure, structural transitions and transport properties are discussed.

## 2. Experimental

Polycrystalline  $\text{Sr}_2\text{YRuO}_6$  and  $\text{Sr}_2\text{ErRuO}_6$  samples were prepared from the appropriate stoichiometric amounts of  $\text{SrCO}_3$ ,  $\text{RuO}_2$ ,  $\text{Y}_2\text{O}_3$  and  $\text{Er}_2\text{O}_3$  at elevated temperature. The thoroughly ground powder mixtures were annealed first at 1173 K for 12 h, and, in a second step, for 48 h, the Y compounds at 1473 K, and the Er compounds at 1513 K. The annealing was done with two intervals of regular grinding. The progress of the reaction and purity of the samples were monitored by powder X-ray diffraction (Cu radiation) using a Philips X'Pert PRO MPD  $\Theta$ - $\Theta$  system equipped with a linear detector (X'Celerator). Neutron diffraction (ND) data were recorded on a high-resolution powder diffractometer for thermal neutrons (HRPT) beam-line located at the Swiss Spallation Neutron Source (SINQ) of the Paul Scherrer Institute in Switzerland. Samples were placed in cylindrical vanadium cans 6 mm in diameter. The measurements were performed with a neutron wavelength of 1.494 Å. Rietveld refinements were done using the Fullprof program [7].

The oxygen content of the samples was determined by the thermogravimetric analysis (TGA) hydrogen reduction method with an atmosphere of 20 vol.%  $\text{H}_2/\text{He}$  and a heating rate of  $20 \text{ K min}^{-1}$  from room temperature to 1100 K, using a Netzsch STA 409 CD thermobalance. The thermal stability of the compounds was simultaneously studied by TG and differential thermal analysis (DTA) measurements during two successive heating/cooling cycles. The samples were heated up to 1073 K at a heating rate of  $20 \text{ K min}^{-1}$  under a gas atmosphere of 20 vol.%  $\text{O}_2/\text{He}$ .

Electron diffraction (ED) studies and high-resolution imaging were performed by TEM using a Philips CM30 with thermoionic gun (at Empa-Switzerland) and in a Tec-

nai F30 with field emission gun (at ETH Zürich, Switzerland), both microscopes operate at 300 kV. ED and high-resolution TEM (HRTEM) simulations were performed using JEMS [8].

The thermal conductivity  $\kappa$  of sintered disc-shaped pellets was calculated from their density  $d$ , thermal diffusivity  $\alpha$  and specific heat  $C_p$ , using the relationship  $\kappa = d \times \alpha \times C_p$ . The thermal diffusivity was measured using a Netzsch LFA 457 laser flash analyser in the temperature range  $T = 300$ – $1273 \text{ K}$ . The specific heat  $C_p$  was determined by DSC using a NETZSCH DSC 404 C Pegasus in a synthetic air atmosphere at a heating rate of  $20 \text{ K min}^{-1}$ .

The electrical transport property measurements were done on a sintered bar-shaped pellet. The electrical conductivity and the Seebeck coefficient were measured in the temperature range  $T = 340$ – $1240 \text{ K}$  in air, using the RZ2001i measurement system from Ozawa Science, Japan. The Seebeck coefficient was measured by the steady-state method while, for electrical conductivity, the DC four-probe method was applied. Two electrical contacts were placed at the ends of the sample and the two others on the sample body. The contacts at the ends were made mechanically with Pt layers. The contacts on the pellet body were made by surrounding the bar-shaped sample with Pt wires.

X-ray absorption spectroscopy at the Ru-L<sub>III</sub> edge was carried out at beamline E4 of the Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronensynchrotron (DESY). The polycrystalline samples were stuck to adhesive tape, which was folded three times to yield the desired increase in absorption of  $\Delta\mu \cdot d \approx 1$ – $2$ . Spectra were recorded at room temperature in transmission mode with a step width of 0.1 eV and a counting time of 2 s per data point. The energy was calibrated against the spectra of Ru metal (2.8380 keV), which was re-measured before and after every five samples as well as after each injection. The WinXAS program was used for data evaluation [9]. Data reduction and fit of the Ru-L<sub>III</sub> edge XANES region were carried out as described in detail in Refs. [10] and [11].

## 3. Results and discussion

### 3.1. Crystal structure and Ru valence state

Fig. 1 shows the Rietveld fit of  $\text{Sr}_2\text{YRuO}_6$  and  $\text{Sr}_2\text{ErRuO}_6$  ND profiles measured at room temperature and the diagram of the structure inset. The crystal structure of both compounds can be derived from  $\text{SrRuO}_3$  perovskite ( $Pnma$  space group) by replacing half the Ru position for  $\text{B}^{3+} = \text{Y}$  or  $\text{Er}$ . Both compounds crystallize in monoclinic structure with space group  $P2_1/n$ , in agreement with earlier reports [12,13]. The unit cell is related to the primitive perovskite unit cell ( $a_p$ ) in the following way:  $a_p = \sqrt{2}a_p$ ,  $b_p = \sqrt{2}a_p$  and  $c = 2a_p$  (subscript p refers to the cubic perovskite structure). The  $\text{Y}^{3+}$  or  $\text{Er}^{3+}$  and  $\text{Ru}^{5+}$  ion are arranged alternately at the B sites of the  $\text{ABO}_3$  perovskite-type structure, i.e., they are

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