Summary of the PhD thesis.

Nowadays, the huge quantity of electricity consumed and the reduction of fossil-fuel reserves are driving research towards alternative energy sources and this is considered one of the main challenges of the 21st century. Today, waste heat is produced in all areas of daily life (in industry, homes and transportation). For example, about 60% of the energy extracted from power plants is lost as waste heat during the generation of domestic electricity. In addition, approximately 40% of the energy produced in a car is wasted as heat and another 30% of the total is used for engine cooling, for a total of 70% of wasted energy. In this scenario, thermoelectrics (TEs) can contribute to be part of the solution to have a more sustainable world, benefiting from thermoelectric generators (TEGs) ability to convert small temperature differences into electrical power, thus obtaining power from wasted heat. In the future, the recycling of heat that would be lost, also known as "energy harvesting", could greatly contribute to reach higher energy efficiencies and reduce CO_2 emissions.

One of the main critical issues in the use of thermoelectric devices for the recovery of waste heat is their stability and resistance to oxidation over time at high temperatures. In fact, most of the common thermoelectric materials are metal alloys or semiconductors that can be easily oxidized at high temperatures. Consequently, the oxidation of the thermoelectric surface leads to the degradation of the generated power and really limits the efficiency and the reliability of thermoelectric modules.

This PhD thesis focuses on the development and evaluation of new oxidation protective coatings for various thermoelectric substrates: higher manganese silicide (HMS, $MnSi_{1.74}$, p-type); Sb doped $Mg_2(Si,Sn)$ ($Mg_2Si_{0.487}Sn_{0.5}Sb_{0.013}$, n-type); titanium suboxide (TiO_x, n-type) and zinc doped tetrahedrite (THD, $Cu_{11.5}Zn_{0.5}Sb_4S_{13}$, p-type).

In the case of HMS, Sb doped $Mg_2(Si,Sn)$ and TiO_x, a range of silica-based compositions were designed, produced and characterized, and subsequently tested as protective glass-ceramic and glass coatings for medium-high temperature thermoelectric modules. The sinter-crystallization behavior of each glass-ceramic was studied in order to select the correct heat treatment of the coating. For Zn doped THD and Sb doped $Mg_2(Si,Sn)$ the effectiveness of commercial hybrid resins was tested as protective coatings in oxidative atmosphere.

The coated samples produced were morphologically and thermo-mechanically assessed before and after oxidation tests. The thermoelectric properties of coated and uncoated TEs were measured before and after ageing and thermal oxidation tests.

The higher manganese silicide was successfully coated with the aim to be used at temperature higher than 500°C. The thermal cycling stability (from room temperature to 600°C in air) of as-sintered and glass-ceramic coated HMS was tested, with respect to changes in their chemical composition and thermoelectric

properties. The reaction between HMS and oxygen at 600°C led to the formation of a Si-deficient layer on the uncoated HMS, and consequently this caused a higher electrical resistivity as well as a reduced power factor. Glass-ceramic coated samples did not show variations in electrical properties compared to the as-sintered one, while they showed a lower electrical resistivity and a higher power factor respect the uncoated ones. The glass-ceramic coating provides thus a successful protection inhibiting the oxidation of higher manganese silicide under thermal cycling. Furthermore, the glass-ceramic coating demonstrated to have self-healing properties at 600°C.

In the case of Sb doped $Mg_2(Si,Sn)$, five new glass-based compositions were designed and characterized, and one of them was found to be able to protect the thermoelectric substrate against oxidation up to 500°C. The morphological and chemical characterization were carried out with the aim to test the efficacy of this type of coating. A good compatibility between the substrate and the coating was demonstrated, with absence of cracks at the interface and within the thermoelectric and the glass-ceramic coating, also after the oxidation test at 500°C for 120 hrs in air. Electric properties will be carried out in the next future to compare the electric performances of an as-sintered Sb doped $Mg_2(Si,Sn)$ with a coated sample after oxidation test, in order to further validate the efficiency of this glass-based system.

A new silica-based glass-ceramic containing titanium oxide was produced in order to protect the titanium suboxide against oxidation up to 600°C and to match TiO_x thermal expansion (CTE ~ $8 \cdot 10^{-6} K^{-1}$). After sinter-crystallization treatment, the glass-ceramic coating softening point was found to be higher respect the parent glass, it was thermo-mechanically compatible with the substrate and it had good wettability on TiO_x. Preliminary oxidation test at 600°C for 48 hrs on coated and uncoated samples are ongoing, therefore they will be published in a follow-up of this PhD thesis.

Two commercial hybrid coatings, cured at low temperature (<300°C), were assessed and one of them (the water-based coating) was successfully used to protect a zinc-doped tetrahedrite thermoelectric. The thermoelectric properties of the uncoated and coated THD, measured after oxidations tests at 350°C and 400°C in air, demonstrated the hybrid coating efficacy in preventing an increase in electrical resistivity and preserving the power factor for coated samples. The results presented in this section are relevant because they represent a novel and easier approach to coatings for TE substrates.

In this PhD thesis critical issues related to the oxidation of thermoelectric substrates and the degradation of their electrical performances have been studied. The design and the development of new glass and glass-ceramics as oxidation protective coatings has been the main focus of this research. For this reason, this PhD work represents a valuable contribution to the integration of advanced engineering ceramics for energy conversion systems and research findings have important implications for developing durable and reliable TE modules.