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Hybrids composites of NCCO/PEDOT for thermoelectric applications

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ABSTRACT

Organic materials are becoming a realistic roadway to fabricate efficient thermoelectric devices using environmental friendly materials. Such requirements are actually fulfilled by thermoelectric generators operating by conducting polymers, but also by hybrid materials. The combination of organic + inorganic compounds may exhibit a high electrical conductivity and Seebeck coefficient as well as lower thermal conductivity in order to efficiently generate thermoelectric power. In these hybrid compounds, perovskite-type oxides are a suitable election for the inorganic part since they have a high Seebeck coefficient although their electrical conductivity is usually low. Blending them with conducting polymers would be a good procedure to improve their thermoelectric properties. In this work, hybrids materials formed by a cobalt perovskite, $Nd_{1-x}Ca_xCoO_3$ (NCCO), have been combined with the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) doped with either poly(styrenesulfonate) (PSS) or tosylate (Tos). The electrical conductivity, Seebeck coefficient, X-ray diffraction and scanning electron microscopy have been used to characterize the resulting material. A thermoelectric power up to 1.0 $\mu W/K^2m$ has been obtained for NCCO/PEDOT:Tos at a 95/5 mass ratio.

1. Introduction

The increasing energy demand in the World's developing countries due to the economic growth, added to the energy curtail produced by the reservoir reduction of fossil fuels has accelerated the development of renewable energy resources. Particularly interesting is the use of thermoelectric (TE) devices, since a thermoelectric generator (TEG) is able to recover waste heat and directly converts it into electricity [1–4]. This phenomenon occurs by means of devices that work without fluids or moving parts making them compact and reliable compared to more conventional engines. However, to build a TEG with enough efficiency to be competitive when compared to other technologies (photovoltaics, wind mills, hydraulic plants, etc), materials with a parameter termed figure of merit higher than unity is required [1,5]. The value of the dimensionless figure of merit (ZT) at a constant temperature depends on the Seebeck coefficient, S, the electrical conductivity, σ, and the thermal conductivity, κ, that is: $ZT = (S^2\sigma T)/\kappa$.

Semiconductor compounds and alloys such as: Bi_2Te_3, PbTe, SiGe and others are being efficiently used in the last twenty years, mainly in high temperature applications [6–9], but several drawbacks have been encountered in most of these inorganic materials such as toxicity, raw material shortages or high costs of production. Clearly, alternative materials must be developed with similar or better ZT.

On one hand, cobalt-oxide-based crystals like Na_xCoO_2, with layered structures and their derivative compounds have been considered extremely good thermoelectric materials achieving ZT values close to 1 or higher. Within this crystal family, we can stand out single crystals of perovskite-type based on transition-metal oxides such as $Sr_{1-x}La_xTiO_3$ [10–13]. These kind of oxides offer large Seebeck coefficients, low electrical conductivity, and relatively low thermal conductivity, although they are not easily synthesizable.

In the last years, organic semiconductors, in particular conducting polymers, are increasingly being employed in electronic and optoelectronic applications such as: solar cells, transistors or supercapacitors [1–17]. They offer important advantages over traditional inorganic semiconductors such as material abundance, low weight, low cost, high toughness and elasticity. They present low thermal conductivity, with improved values of ZT, but unfortunately S and σ are low [1]. In principle, the low electrical conductivity can be improved by doping [18,19], that

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is by changing the free-carrier concentration and mobility. Among the family of conducting polymers, PEDOT is one of the most interesting conducting polymers used at the moment [20,21]. However, although many attempts have been made to increase the Seebeck coefficient of PEDOT, the results are not very promising [22].

On the other hand, a good alternative is to blend metal oxides, particularly perovskite-type oxides, with conducting polymers just making an inorganic-organic hybrid material [23,24]. The conductive polymer will contribute with easy way of production, good mechanical properties, low thermal conductivity and a relatively good electrical conductivity, while the perovskite-type material will supply the high Seebeck coefficient.

The aim of this work is to fabricate hybrid composites to be used as thermoelectric materials. We have selected $Nd_{1-x}Ca_xCoO_3$ (NCCO), a cobalt-based perovskite, as inorganic material since it has a high Seebeck coefficient and it can be easily obtained in the laboratory with different stoichiometries. PEDOT:PSS and PEDOT:Tos, i.e. PEDOT doped with two different counter-ions, are the two conducting polymers selected to increase the electrical conductivity of the perovskites while at the same time they are used as a kind of plasticizer. Thus, the motivation to make a hybrid nanocomposite is to find the proper amount of each material in order to attain the best compromise between the electrical conductivity and the Seebeck coefficient, actually the best power factor. The crystal particles of $Nd_{1-x}Ca_xCoO_3$ have been synthetized

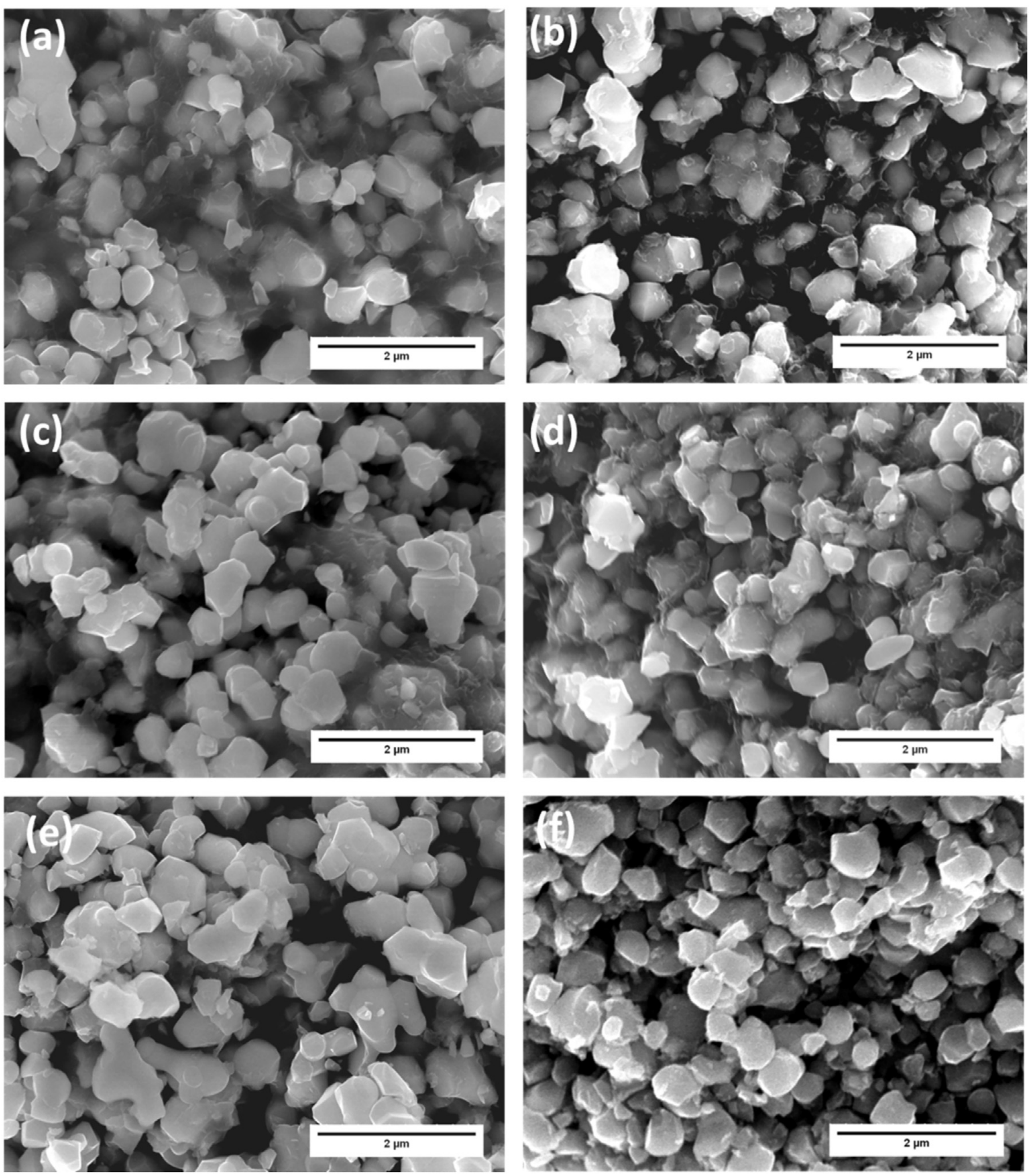

Fig. 1. SEM images of NCCO/PEDOT:PSS composites with a (a) 80% (c) 90% and (e) 95% of $Nd_{0.999}Ca_{0.001}CoO_3$. SEM images of NCCO/PEDOT:Tos composites with an (b) 80% (d) 90% and (f) 95% of $Nd_{0.999}Ca_{0.001}CoO_3$.