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Structural, magnetic and transport properties of 2D structured perovskite oxychalcogenides

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ABSTRACT

We have been looking for new potential thermoelectric materials in the family of 2D structured perovskite oxychalcogenides containing $[Cu_2Ch_2]^{2-}$ blocks (Ch = S or Se). Using high temperature syntheses, a new oxyselenide Sr_2CuFeO_3Se has been isolated and its structure has been compared to the isotypes sulfides, Ca_2CuFeO_3S and Sr_2CuFeO_3S, prepared by the same technique. By combining powder XRD and TEM analyses their composition and structure were analyzed. They all three crystallize in the Sr_2CuGaO_3S-type structure, with only the oxyselenide showing a Fe deficiency which is related to the stacking faults evidenced by high resolution TEM. Transport and magnetic properties of the samples have been studied; especially their electrical resistivity is characterized by high values in the range from 1 to 10 kΩ cm at 300 K. Thermoelectric potential of these materials is also discussed.

1. Introduction

This contribution is part of an on-going research aiming at discovering new efficient thermoelectric materials, to harvest waste heat sources in order to generate electrical power. The thermoelectric efficiency of a material is described by its figure of merit ZT defined as $\alpha^2T/\rho(\kappa_{el} + \kappa_{lat})$, where T is the absolute temperature, α the Seebeck coefficient, ρ the electrical resistivity, κ_{el} the electronic contribution to the thermal conductivity and κ_{lat} the thermal conductivity of the lattice (phonons).

In the past, numerous metal transition oxides of layered structures have attracted much interest because of their structural relationships with the high-T_c superconducting cuprates [1]. The latter are commonly described as some regular intergrowths between some perovskite blocks and some RS-type slices (RS = rock salt). The 2D structured oxychalcogenides combining anti-fluorite layers with others 2D building blocks were mainly studied for their transparent semiconducting properties [2–4], until the recent discovery of superconductivity in the oxypnictide (*Ln*O)FeAs [5], and then in the phases derived from the Fe_2Se_2 layered materials [6,7], which has renewed the interest for the search of new materials containing M_2Ch_2 layers. Another interesting point is that the layered oxychalcogenides exhibit common structural feature with a recently discovered promising thermoelectric materials BiOCuSe [8], which belongs to the structural family of ZrSiCuAs 1111 type compounds [9], built from a conducting Cu_2Se_2 layers stacked with insulating Bi_2O_2 layers. Similarly to iron based superconductors, their interesting electrical transport properties are grounded in the layered structure: the electronic conduction lies in the 2D character of the M-Ch layer whereas the separating layers act as charge reservoir controlling the doping of the former.

In that respect, the materials studied here are potentially interesting 2D materials. They are generally formulated AE_2MO_3-CuCh (where AE is an alkaline earth, M is a 3d metal and Ch is S or Se) and they crystallize with the Sr_2CuGaO_3S-type structure [10] (Fig. 1) which is built from a 1:1 regular intergrowth between perovskite slabs and anti-fluorite chalcogenides Cu_2Ch_2 layers. The perovskite based layer is made of square–pyramidal MO_5 polyhedra. The good geometrical and charge compatibilities of the rigid layer $(Cu_2Ch_2)^{2-}$ with the metal perovskite oxide layer $[(MO_2)(AEO)(AEO)(MO_2)]^{2-}$ is stabilized by Sr^{2+} cation layers connecting these two types of structural blocks (Fig. 1). While for BiOCuSe the oxide layer which acts as charge reservoir is isostructural to the conducting layer, in our case the Cu_2Ch_2 layers are separated by perovskite like layers and Sr layers, as described above.

Aside BiOCuSe, few oxychalcogenides have been studied for their thermoelectric properties. In order to screen for new promising materials for thermoelectric applications, we have synthesized some 2D oxychalcogenides related to the generic AE_2MO_3CuCh series assuming AE = Sr,Ca and Ch = Se.

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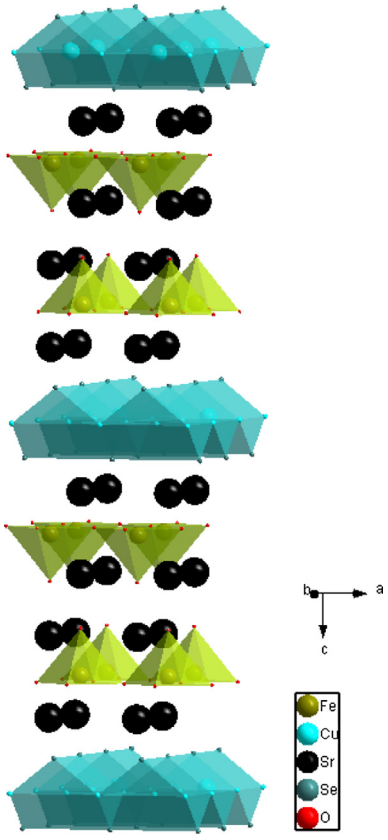

Fig. 1. View of the crystal structure of Sr_2CuFeO_3Se.

We present here, three oxychalcogenides prepared by solid state route and high temperature synthesis, and we show their electrical and magnetic properties.

2. Experimental details

2.1. Synthesis

In order to prevent oxidation of reactants and products, all manipulations are performed under vacuum (sealed tubes) or inert gas (glove box or sealed containers). In the present experiments, the starting materials were home-made strontium based materials SrSe or SrS, used with the appropriate amounts of commercials SrO_2, Cu and FeO. In the same way for calcium based material, the following starting materials were used: CaO, Cu, FeO and S. Typically for each batch, one gram of powder was prepared, pressed into pellets and sealed into a fused silica tube before being annealed at 850 °C for 10 h. Additional regrinding and annealing were processed in order to ensure homogeneity of the samples.

2.2. Powder X-ray diffraction

Quality of the samples was checked at each annealing step by means of X-ray powder diffraction using an X-Pert Pro Panalytical diffractometer equipped with an 1D PIXcel detector. The structural Rietveld refinements of the various samples have been performed using FULLPROF [11] program included in the WinPLOTR [12] Package. The peaks profile has been modeled with a pseudo Voigt function and the background contribution has been defined from a set background points with refinable intensity.

2.3. Transmission electron microscopy

In order to test the crystal structure quality of the synthesized compounds and to confirm their structure, a transmission electron microscopy (TEM) study was performed with a Tecnai G2 30 UT microscope operating at 300 kV and having 0.17 nm point resolution (Cs = 0.7 mm). Energy dispersive X-ray (EDX) analysis was performed inside the TEM by using an EDAX analyzer. The TEM samples were prepared by grinding sample in an agate mortar in methanol and then by depositing the powder/solvent mixture on nickel holey carbon grid. High resolution TEM (HRTEM) image simulations have been carried out with the MacTempas and CrystalKit softwares.

2.4. Magnetic measurements

The magnetic characterizations were made by using an SQUID magnetometer (Quantum Design). For that purpose, fresh bars, just taken out of the glove box, were used. The data were registered upon warming in 10^{-2} T from 5 K to 300 K after zero field cooling and then field cooling processes.

2.5. Transport property measurements

Silver paste was used to deposit electrical contacts on fresh bars for four probe measurements of the resistivity (ρ). A steady state technique based on homemade sample pucks for the Seebeck coefficients (S) measurements with the same type of electrical contacts was employed. All these ρ and S measurements were performed in a Quantum Design Physical Properties Measurement System upon cooling from 300 K to 5 K. It must be mentioned that the ρ data were limited to values below about 10^6 Ω cm whereas for ρ values greater than ~10^5 Ω cm, S values were not measurable due to the too high sample impedance compared to the voltmeter internal impedance.

3. Results and discussion

3.1. Structural part

Three different samples were analyzed: the new oxyselenide Sr_2CuFeO_3Se and the two already reported isotypic sulfides compounds Ca_2CuFeO_3S [13] and Sr_2CuFeO_3S [14]. All three compounds crystallize with the Sr_2CuGaO_3S-type structure (space group P4/*nmm*) (Fig. 1). Ca_2CuFeO_3S has recently been reported to be the first layered chalcogenide perovskites involving calcium [11]. The purity of three samples is confirmed by the experimental X-ray diffraction patterns as shown on Fig. 2. Structural Rietveld refinements from the powder XRD patterns have been performed and leads to the following cell parameters, $a = 3.9010(1)$ Å and $c = 15.6380(3)$ Å for Sr_2CuFeO_3S, $a = 3.8296(5)$ Å and $c = 14.9606(1)$ Å for Ca_2CuFeO_3S, and $a = 3.9367(2)$ Å and $c = 15.9701(7)$ Å for Sr_2CuFeO_3Se. These cell parameters differences are consistent with the ionic radius [$r(Sr^{2+}) > r(Ca^{2+})$ and $r(Se^{2-}) > r(S^{2-})$]. Rietveld refinements lead to satisfactory reliability factor for the oxysulfides (See Tables 1 and 2). For the non-previously reported compound Sr_2CuFeO_3Se, the refinement has been carried out considering a predicted structure isotype to the sulfides counterpart (See Table 3). If the oxysulfide Sr_2CuFeO_3S seems to be monophasic since its whole pattern is fully indexed, some extra peaks are detected in the cases of the Ca_2CuFeO_3S and the new oxyselenide Sr_2CuFeO_3Se (black arrows on Fig. 2). Despite many attempts to synthesize a single phase sample of Sr_2CuFeO_3Se, we observe systemically the $Cu_{1.8}Se$ phase as secondary phase. In order to clearly evidence the crystal chemistry of