Experimental Report

Proposal: **5-23-656** **Council:** 10/2012

Title: Resistivity anomaly in the BiCuSeOsystem

This proposal is resubmission of: 5-23-652

Researh Area: Materials

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Samples: BiCuSeO
BiCu(Se0,8Te0,2)O
(Bi0,975Sr0,025)CuSeO
(Bi0,85Sr0,15)CuSeO

Instrument	Req. Days	All. Days	From	To
D20	4	4	17/05/2013	21/05/2013

Abstract:

BiCuOSe, which crystallizes in the same structure as LaFeAsO, is a new promising thermoelectric material. During previous experiments on these samples, we have observed an electrical resistivity anomaly. From our XRD study, it seems that this anomaly cannot be ascribed to structural changes, and magnetic susceptibility measurements have not been conclusive. However it is very similar to other results obtained for LaFeOAs. For this latter material, the anomaly can be attributed to the emergency of a spin-density-wave coupled to a structural transition. As preliminary experiments have shown additional peaks below the anomaly temperature in neutron diffraction patterns, we propose to use neutron powder diffraction to study the evolution of this anomaly between doped and undoped compounds in order to understand its origin.

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For a couple of years, the research activities of our team in ICMMO are partly devoted to the study of BiCuSeO-based oxychalcogenides, which are very promising thermoelectric materials (we have shown that they exhibit the largest thermoelectric figure of merit ever reported for p-type Pb-free bulk thermoelectric materials in the medium temperature range).

Beside these promising thermoelectric performances, we have evidence during our study that they also exhibit interesting physical properties, in particular transport properties anomalies at low temperature that could have been linked to magnetic or structural transitions. Indeed, we had observed during a preliminary neutrons diffraction experiment the presence of small peaks in the BiCuSeO diffraction pattern below about 250K that did not correspond to nuclear peaks of the P 4/nmm space group.

The main objective of these neutrons diffraction experiments was to record the neutrons diffraction patterns of several BiCuSeO-based samples as a function of temperature at two distinct wavelength, in order to obtained new clues for the understanding of the electrical transport anomalies in this system.

The studied compositions were BiCuSeO (which exhibits an anomaly of the electrical resistivity around 250K), BiCuTeO, and several samples belonging to the solid solution BiCuSeO-BiCuTeO (although BiCuSeO and BiCuTeO exhibit a metallic behavior of the electrical resistivity, there is an unexpected evolution to a semiconductor behavior for intermediate compositions in the range Te=10% to 50%).

As it can be seen in figure 1, no supplementary peak appears in the diffraction pattern of BiCuSeO between 5K and 300K. This result was somehow unexpected as our preliminary measurements had evidenced two supplementary peaks below 240 that did not correspond to nuclear positions. It means that these peaks were most probably artefacts of measurement, as the XRD and neutrons diffraction patterns of the sample at room temperature did not evidence any secondary phase (sample holder? Cooling system?). On the one side these observations might be disappointing, but on the other side it enables us to eliminate antiferromagnetic ordering as a possible cause for the observed electrical conductivity anomaly (as was observed in LaFeAsO, parent compound of the iron-arsenide superconductors, which shares the same crystal structure as BiCuSeO). Moreover, the evolution of the lattice parameter as a function of the temperature, figure 2, (and of the atomic positions, not shown) does not evidence any anomaly or particular feature.

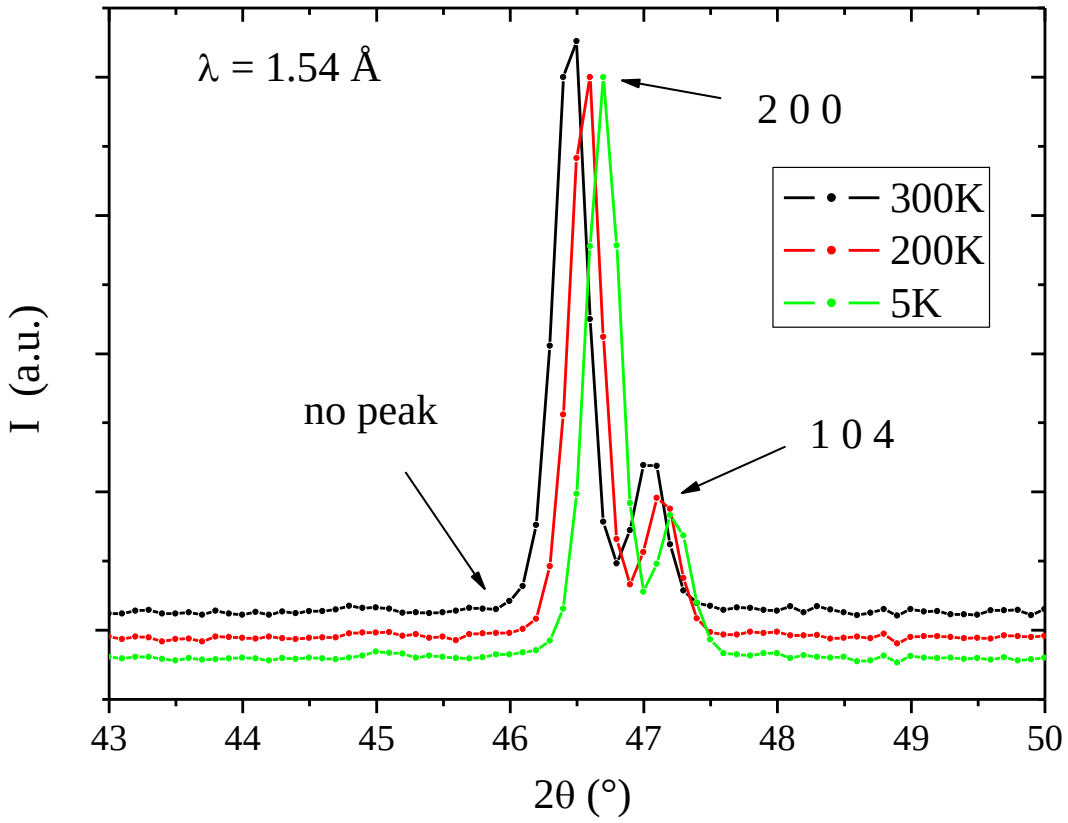

Figure 1: Magnified view of the area where a supplementary peak could be observed in our preliminary neutrons diffraction experiments.

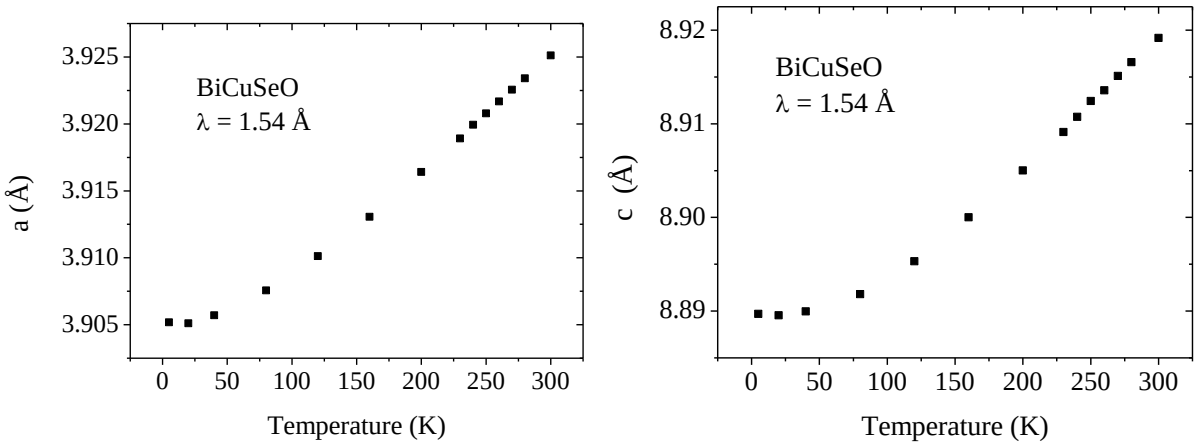

Figure 2: Temperature dependence of the lattice parameters. No anomaly can be observed around 240-260K, temperature corresponding to the anomaly of the electrical resistivity in this compound.

We have also recorded the temperature dependence of the diffraction patterns of several samples belonging to the BiCuSeO-BiCuTeO solid solution (Te substitution suppressed the electrical resistivity anomaly in BiCuSeO, and the electrical behavior of substituted samples in the Te=10% to 50% range is surprisingly different). No significant feature was observed neither in the temperature dependence of the structural parameters for the various samples, nor in the evolution of the structural parameters with Te fraction (as exemplified in figure 3 with the evolution of the Cu*Ch*$_4$ tetrahedra angles with Te fraction).

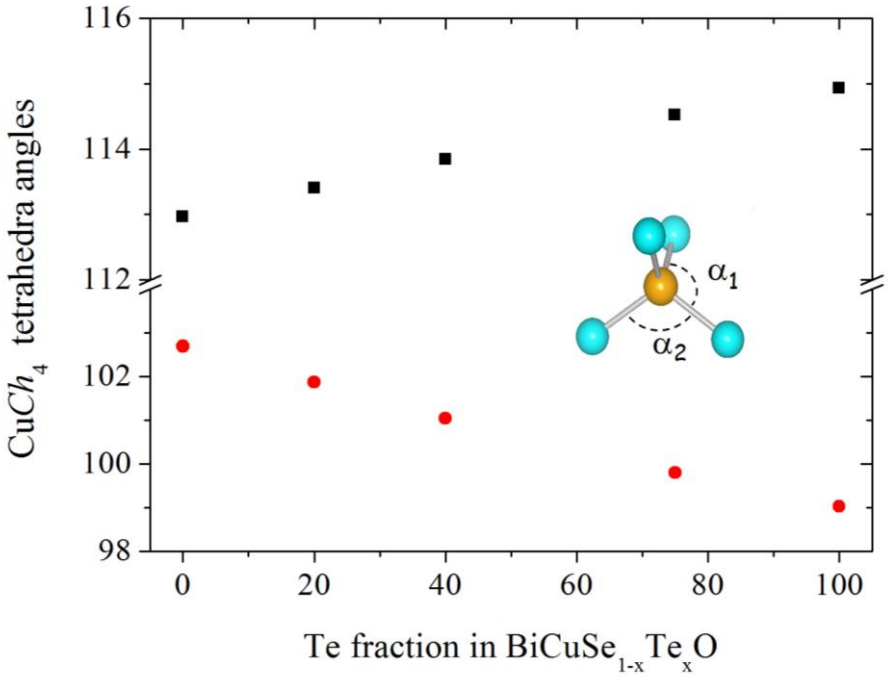

Figure 3: Cu*Ch*$_4$ tetrahedra angles evolution with the Te substitution in the BiCuSeO-BiCuTeO solid solution.

Although these experiments did not enable us to understand the origin of the electrical transport anomalies observed in this system we will in the near future:

- Use the temperature dependence of the structural parameters of BiCuSeO obtained here in our study of the origin of the anomalously low lattice thermal conductivity observed in this material, which is the object of an ANR proposal submitted in May 2014 (they will be used as starting basis and references for ab-initio calculations, for the estimation of the elastic properties, and as starting basis for an INS study)
- Include the data obtained here about the BiCuSeO-BiCuTeO solid solution in a "wider" publication that will include neutrons diffraction, HR-XRD (synchrotron), XAS and simulations.