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Phonon mode softening at the ferroelectric transition in EuxBa1-xTiO3

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151Eu Mössbauer study of phonon softening in ferroelectric EuxBa1-xTiO3.

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Summary

The ferroelectric EuxBa1-xTiO3 system is being studied as part of a project to search for the permanent electric dipole moment of the electron [1]. Part of this work involves understanding the materials properties of the system. Doping BaTiO3 with europium drives the ferroelectric transition down from 278 K [2] at x=0, to 0 K by x<0.75. The Eu-doped materials are weakly conducting, so detecting the ferroelectric transition by either capacitive methods or bulk susceptibility is difficult, however the phonon mode softening that accompanies the formation of the orthorhombic ferroelectric phase leads to a characteristic reduction in the Mössbauer-Lamb (or "f")-factor [3]. 151Eu Mössbauer measurements on two samples of Eu0.5Ba0.5TiO3 have confirmed the presence of the phonon mode softening centred at 180 K, but also revealed an unexpected result. The signal from divalent europium (Eu2+) dominates the spectra of both samples; however, we found that 9-12% of the europium was present as Eu3+. While initially ascribed to unreacted Eu2O3, neither xrd nor neutron diffraction showed any evidence for this, or any other trivalent europium impurity. More surprisingly, the temperature dependence of the f-factor shows a much stronger response in the Eu3+ component than in the Eu2+ one, clearly indicating that the trivalent europium is present within the Eu0.5Ba0.5TiO3 phase and ruling out any possibility of phase separation or impurity effects. Preliminary analysis of neutron powder diffraction data rules out the possibility that some of the europium might be located on titanium sites and the origins of the enhanced phonon softening at the Eu3+ site remain unclear.

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