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Report:

We investigated the ferroelectric phase transition in multiferroic $Ge_{1-x}Mn_xTe$ thin films. Multiferroics, materials combining ferroelectric (FE) and ferromagnetic (FM) order in one and the same material, have triggered immense interest [1] because of their unique properties and device applications [2]. Single phase materials that show simultaneously FE and FM are, however, very rare. $Ge_{1-x}Mn_xTe$ is a material in which these two properties coexist for a certain range of temperatures and Mn contents. FM interactions between the Mn ions are mediated by mobile carriers, resulting in FM transition temperatures above 150 K, which are amongst the highest of all diluted FM semiconductors. The host material GeTe is a narrow gap semiconductor as well as one of the simplest ferroelectrics with only two atoms per primitive unit cell [3]. It undergoes a spontaneous paraelectric to FE phase transition at a temperature of ~625K [3], below which the Fm3m space group symmetry of the cubic rock salt phase (shown in Fig. 1a) is broken and a polar, rhombohedral R3m structure is formed by elongation of the unit cell along a <111> body diagonal (see Fig. 1a). Due to the relative displacement of the Ge and Te sub-lattices by about 0.35 Å along this direction [3] a spontaneous FE polarization appears. Recently, the coupling between magnetisation and FE domains, i. e. multiferroic behaviour of $Ge_{1-x}Mn_xTe$ has been established by FM resonance experiments [4].

Thin films of $Ge_{1-x}Mn_xTe$ with thicknesses of 500 nm and composition from x = 0 to 0.4 (for higher Mn concentration phase separation occurs [5]) grown on $BaF_2(111)$ substrates by molecular beam epitaxy (MBE) [5] were investigated. In our original proposal we suggested to use the X-ray standing wave method to probe the change of the shift of the different sublattices occuring at the ferroelectric transition. However, during one of our synchrotron experiments (HC1424), performed after the submission of the proposal, on a similar material system it turned out that X-ray standing wave measurements are unlikely to be successful due to high mosaicity of the thin films and high fluorescence signal from the substrate.

In discussion with the local contact it turned out that the assigned beamline allowed us to use X-ray diffraction with a 2D detector to measure the diffracted intensity of several peaks in 3D as function of the temperature. The diffraction peaks are sensitive not only to the unit cell deformation (peak position) during the transition, but also to the position of the atoms (peak intensities).

We investigated a set of 5 samples with different Mn composition ranging from 0 to 40%. For every sample we investigated the temperature range from ~80K (minimum achievable) to 750K. Using 20keV photons we mapped the 3D intensity around 4 diffraction peaks ((222), (333), (331), (224)) at various temperatures. Analysing the diffraction peak positions we obtain the unit cell parameters of the thin film and of the substrate. The variation of these parameters vs. temperature is shown in Fig. 1 b,c. The unit cell angle shows a clear kink at the transition. The lattice parameter itself is does not show a pronounced change at the transition, however, the thermal expansion properties are slightly changing resulting in a weak change of the slope. The variation of the integrated diffraction intensities of the investigated Bragg peaks gives us an indication about the shift of the sublattices, since they only very weakly depend on the lattice parameter and unit cell angle. Especially the intensity ratio of the (222) and (333) peak is very sensitive to the shift of the the Te atoms along the [111] direction which is the main polarization axis in the thin films. In Fig. 2 we show the intensity ratio of the (333) and (222) peak as contour plot vs. the Mn-composition and temperature in comparison with a contour plot of the unit cell angle. Both contour plots show the same main features indicating a correlation between the shift of the atoms and the ferroelectric transition. Quantitive analysis of the intensity ratio, which will result in an estimate of the absolute shift of the atoms vs. temperature is ongoing.

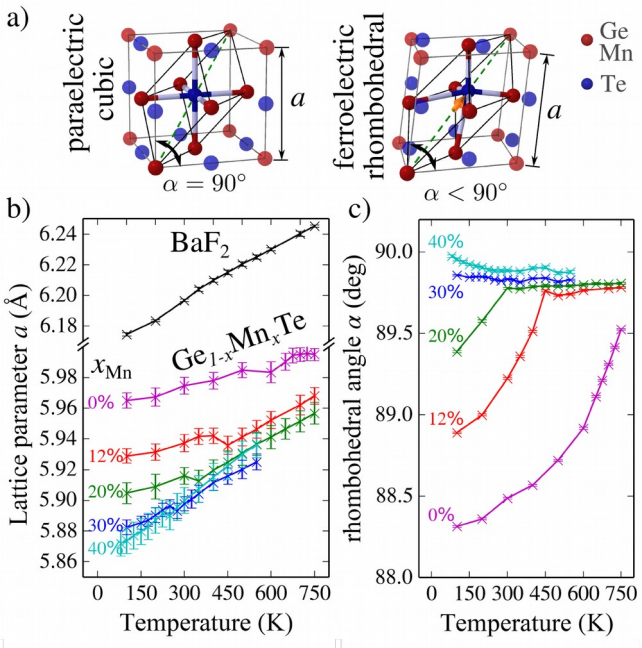

Figure 1: a) Sketch of the unit cell of (Ge,Mn)Te in the paraelectric cubic and rhombohedral distorted ferroelectric phase. b) Variation of the lattice parameter with temperature for both the thin films of GeMnTe and the BaF2 substrate. c) Unit cell angle as indicated in panel a) showing the deformation of the unit cell at the ferroelectric transition.

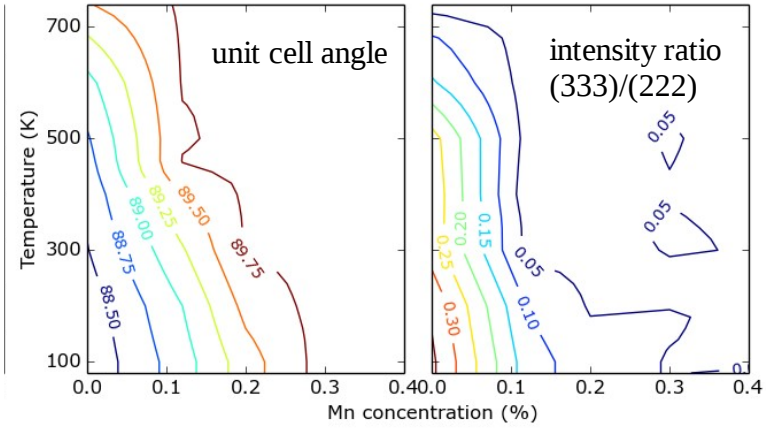

Figure 2: Contour plots of the unit cell angle (left) and intensity ratio of the (333)/(222) Bragg peaks (right). The similarity of the two panels indicates the correlation of the shift of the Te sublattice and the unit cell deformation.

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