Morphotropic phase boundary in ferromagnets - a way leading to large magnetostriction

The morphotropic phase boundary (MPB), a phase boundary separating two ferroelectric phases of different crystallographic symmetries in the composition-temperature phase diagram, is crucial in ferroelectric materials, because MPB can lead to a great enhancement of piezoelectricity, the most useful property of this large class of functional materials. The current workhorse of piezoelectric materials, i.e., PZT ($PbZrO_3$-$PbTiO_3$) and PMN-PT ($PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$), is designed to have a composition close to the MPB to achieve a maximum piezoelectric effect. Figure 1(a) shows a typical ferroelectric MPB in PZT, which separates a ferroelectric rhombohedral (R) phase on the $PbZrO_3$ side and a ferroelectric tetragonal (T) phase on the $PbTiO_3$ side. The R and T ferroelectric phases share a common cubic paraelectric phase at high temperatures. Theoretical and experimental studies have shown that, at the MPB composition, $\boldsymbol{P_s}$ can be easily rotated under a small external field, thereby causing a high piezoelectric effect.

Ferromagnetic systems are physically parallel to ferroelectric ones; the former involve an ordering of magnetic moment and the latter involve an ordering of polarization below a critical temperature (Curie temperature) T_c. In both systems, the order parameter is coupled to the lattice, respectively leading to the magnetoelastic and piezoelectric effects. From the physical parallelism between ferromagnetism and ferroelectricity, it is tempting to ask an interesting question: Can a similar MPB situation exist in ferromagnetic systems? If yes, can such magnetic MPB yield large magnetostriction (magnetic-field-induced distortion, an effect analogous to the piezoelectricity in ferroelectrics)? Following the definition of MPB in ferroelectrics, a magnetic MPB should be a phase boundary separating two different ferromagnetic states with different crystallographic symmetries.

So far, the major obstacle to the existence of MPB in ferromagnets has been the general observation (by conventional X-ray diffractometry (XRD)) that a difference in $\boldsymbol{M_s}$ direction does not result in a difference in crystal symmetry, differently from the ferroelectric case. Therefore, for ferromagnetic systems, the condition for MPB seems not satisfied. However, with the great enhancement in the structure resolution using synchrotron XRD (**BL15XU**), recent studies have proved that different ferromagnetic states indeed correspond to different crystal symmetries

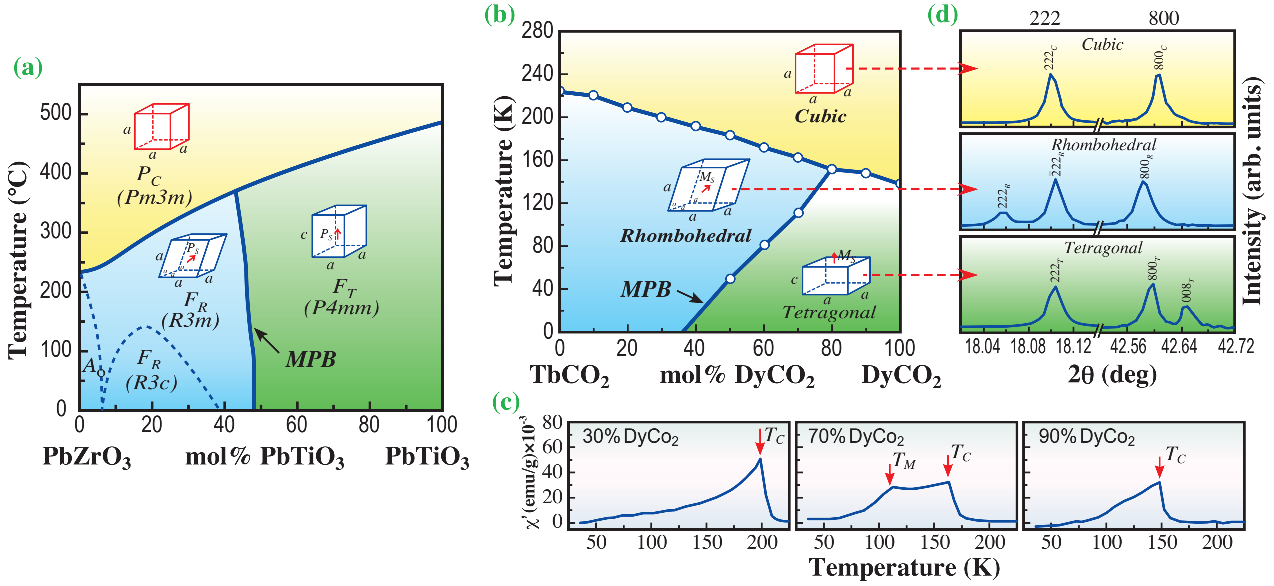

Fig. 1. **(a)** Phase diagram of PZT. **(b)** Phase diagram of $TbCo_2$-$DyCo_2$. **(c)** Temperature dependence of ac susceptibility χ'. T_c and T_M denote the para-ferro and ferro-ferro transition temperatures, respectively. **(d)** Synchrotron XRD profiles of cubic paramagnetic, rhombohedral ferromagnetic and tetragonal ferromagnetic phases.

[1,2], the same as in the ferroelectric case; however, the lattice distortion due to a difference in crystal symmetry is usually too small to be detected by conventional XRD analysis.

Now, we have a good reason to expect the existence of a magnetic MPB and therefore we propose to detect a magnetic MPB in a pseudo binary ferromagnetic system $TbCo_2$-$DyCo_2$, using of BL15XU beamline. The results are shown in detail in Fig. 1, Fig. 2, and Fig. 3. The MPB composition demonstrates a 3-6 times larger "figure of merit" of magnetostrictive response than the off-MPB compositions (Fig. 3). The finding of MPB in ferromagnets may help to discover novel high-performance magnetostrictive and even magnetoelectric materials [3].

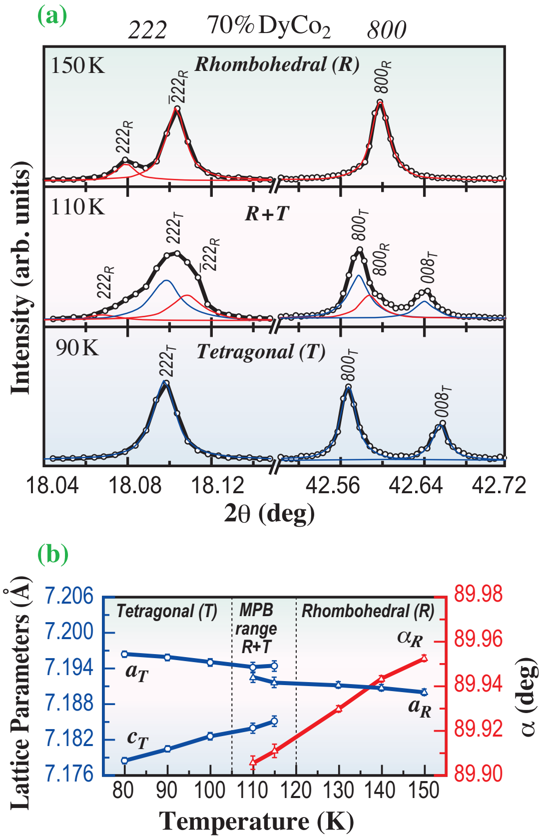

Fig. 2. **(a)** XRD profiles of rhombohedral phase at 150 K (above MPB), a mixture of rhombohedral and tetragonal phase at 110 K (at MPB), and tetragonal phase at 90 K (below MPB). The red and blue peaks underneath the experimental peaks are Lorentzian rhombohedral and tetragonal peaks respectively, giving the best fit to the experimental profiles. **(b)** Temperature dependence of lattice parameters (a_R and α_R stand for the lattice parameters of the R-phase with M_s||[111], and a_T and c_T for that of the T-phase with M_s||[001]); the MPB corresponds to a 2-phase mixture of rhombohedral and tetragonal phases. The error bars are determined by the fitting error in Fig. 2(a).

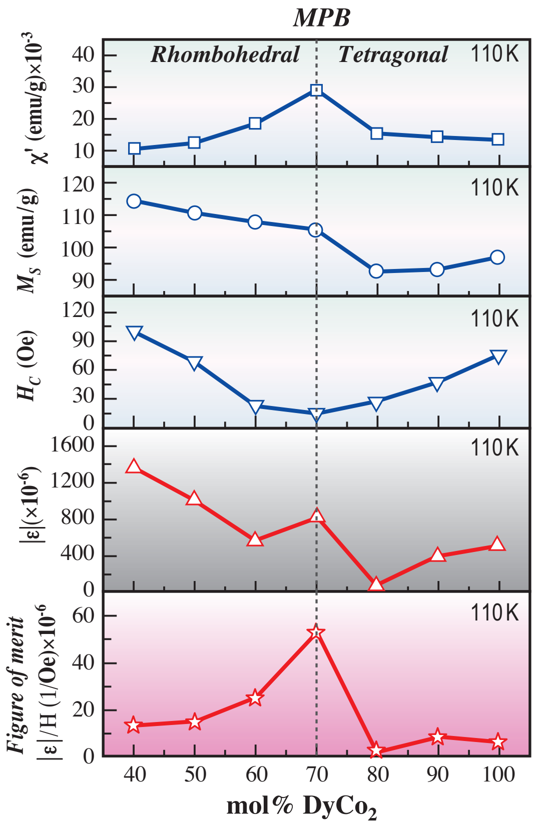

Fig. 3. Composition dependences of Ac susceptibility χ', saturation magnetization M_s, coercivity H_c, magnetostriction ε (absolute value) at 10 kOe field, and figure of merit ε/H_c, in relation to MPB composition at 110 K.

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