

m36.p04

Beating the Miscibility Barrier Between Iron Group Elements and Magnesium by High-Pressure Alloying

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Keywords: high-pressure, alloying, iron, magnesium

It is now generally recognized that all metals and compounds show some solubility in the solid or liquid state, but the extend of solid solubility is different in different cases. In particular, Fe and Mg are almost immiscible at ambient pressure. There is clear evidence that they do not mix even in the liquid state at ambient pressure. Different paths are exploited nowadays to synthesise alloys between immiscible elements, e.g. mechanical alloying by means of ball milling or thin film alloying using deposition techniques. In our Letter we suggest an alternative path for overcoming miscibility barrier via high-pressure alloying, a possibility of which is predicted in our *ab initio* calculations.

In order to test theoretical predictions, and to prove a formation of alloys between immiscible elements at high pressure, a novel experimental methodology has been developed, internal electrical heating. It allows us to overcome such deficiencies of known methods as low temperature supply of external electrical heating and inhomogeneous heating of mixture of metals by lasers. In particular, we conducted successful experiments on alloying Fe, Co, and Ni with Mg. The pressure range (over 125 GPa) at which alloying experiments now become available increased about 4 to 5 times in comparison with common multi-anvil apparatuses. This should be of particular interest for geophysics and geochemistry communities.

Our main result, a possibility of alloying between Fe and Mg, is also in direct relevance for understanding the composition of the Earth's core. Indeed, the Earth's outer core is a geochemical parameter crucial for understanding the evolution and current dynamics of our planet. Since it was recognized that the liquid metallic outer core is about 10% less dense than pure iron, different elements lighter than iron, including Si, S, O, C, and H, were proposed as major or at least significantly abundant in Earth's core. However, combination of experimental results with theoretical and geochemical considerations shows that it is unlikely that any one of these elements can account for the density deficit on its own. Our observations suggest that magnesium can be an important light element in Earth's outer core. Moreover, magnesium is not simply one more element in a long list of light elements proposed to be present in the Earth core. It is one of the most abundant on the Earth elements which *never* was seriously considered to be incorporated into the core because at *ambient conditions* magnesium simply does not alloying with iron, assumption clearly failed in view of our work.

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Low-symmetry structures in the Zr-rich side of the pressure-temperature-composition phase diagram of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$

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Keywords: lead zirconate titanate (PZT), neutron diffraction, phase diagram

The recent discovery by B. Noheda *et al.* [1] of a monoclinic phase, near the morphotropic phase boundary of the lead zirconate titanate $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ system, has prompted renewed interest in structural studies of this technologically important perovskite solid solution. Indeed, the presence of this low symmetry structure with *Cm* space group, in this very narrow region of the phase diagram between the ferroelectric tetragonal and rhombohedral forms, provides a possible explanation for the high piezoelectric response of this ceramic material, since the direction of the polarization can lie anywhere between the pseudocubic [111] and [001] directions [2]. Additionally, several low-symmetry intermediate structures have been observed close to the morphotropic phase boundary and close to the antiferroelectric-ferroelectric phase boundary, resulting in a decrease in the stability field of the rhombohedral form. Therefore, we decided to re-investigate the stability field of the rhombohedral phase by studying two Zr-rich compositions: $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$ and $\text{PbZr}_{0.7}\text{Ti}_{0.3}\text{O}_3$. We have performed neutron and X-ray diffraction, Raman spectroscopy and dielectric measurements in situ as a function of the temperature (1.5K to 300K) and the pressure (atmospheric pressure to 10GPa). Neutron data were analysed in detail by Rietveld refinement. Different models were tested and compared for each data set. Surprisingly, the structure of $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$ at room temperature is not rhombohedral but monoclinic. The best fit is obtained with a two-phase model with space groups *Cm* and *Cc*. Furthermore, we demonstrate that the ferroelectric low temperature phase is actually monoclinic with space group *Cc*. Concerning high pressure behaviour of the solid solution, x-ray diffraction indicates that $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$ undergoes an extra phase transition, with unit cell doubling, in comparison with $\text{PbZr}_{0.7}\text{Ti}_{0.3}\text{O}_3$. This is easily understood considering that the unit cell of $\text{PbZr}_{0.7}\text{Ti}_{0.3}\text{O}_3$ is already doubled at atmospheric pressure. First results of neutron diffraction measurements show that additional low-symmetry phases are encountered at high pressure for $\text{PbZr}_{0.6}\text{Ti}_{0.4}\text{O}_3$.

[1] B. Noheda *et al.*, Appl. Phys. Lett. 74, 2059 (1999).

[2] R. Guo *et al.*, Phys. Rev. Lett. 84, 5423 (2000).