

MAR11-2010-000740

Abstract for an Invited Paper  
for the MAR11 Meeting of  
the American Physical Society

### High-pressure Synthesis and Magnetic Properties of 4d and 5d Transition-metal Oxides<sup>1</sup>

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The pressure effect on synthesis of oxides with perovskite  $ABO_3$  and perovskite-related structures has become more clear in recent years. The geometric tolerance factor  $t \equiv (A-O)/\sqrt{2}(B-O)$  measures the structural stability. High-pressure synthesis enlarges the range of the  $t$  factor where the perovskite structure can be stabilized. For the  $ABO_3$  compounds with  $t > 1$ , high pressure reduces the  $t$  factor since the A-O bond is more compressible than the B-O bond. Therefore, perovskite would be the high-pressure phase for ambient-pressure polytype structures. However, the bonding compressibility argument is no longer valid for the  $ABO_3$  with  $t < 1$ . A  $dt/dP > 0$  is normally obtained for  $t$  less than but very close to 1, *i.e.* the orthorhombic distortion becomes smaller under pressure. For those highly distorted perovskites with  $t$  factor far less than one, pressure enlarges further the orthorhombic distortion and eventually leads to a phase transition to the post-perovskite phase. As for  $PbRuO_3$ , high pressure prefers the small-volume perovskite phase relative to a competitive pyrochlore phase  $Pb_2Ru_2O_7$ . Understanding the pressure effect and the new capacity provided by a Walker-type multianvil press enabled us to expand the perovskite family and to obtain new phases of 4d and 5d oxides. Studies of these new 4d and 5d oxides allow us not only to address long-standing problems, but also to explore exotic physical properties. (1) In the perovskite  $ARuO_3$  (A= alkaline earth), we have completed the phase diagram from A= Ca to Sr and to Ba and also accounted for the A-cation size-variance effect. A systematic study of the Curie temperature  $T_c$  and the critical behavior as a function of the average A-site size and the size variance as well as external high pressures reveals explicitly the crucial role of the lattice strain on the ferromagnetism. The mean-field critical behaviour near  $T_c$  found previously in  $SrRuO_3$  is not typical of these perovskite ruthenates.  $T_c$  is completely suppressed by Pb doping in  $Sr_{1-x}Pb_xRuO_3$  not due to the steric effect, but to the orbital hybridization between  $Pb^{2+}$  6s and  $Ru^{4+}$  4d. As the end member, metallic  $PbRuO_3$  undergoes a first-order phase transition to a metallic *Imma* phase at  $T_t \approx 90$  K. (2) A new polytype phase 5H has been synthesized under a narrow pressure range, which fits the structural sequence along with other polytypes 9R, 6H and 3C of  $BaIrO_3$ . The ground states of these  $BaIrO_3$  polytypes evolve from a ferromagnetic insulator with  $T_c \approx 180$  K in the 9R phase to a ferromagnetic metal with  $T_c \approx 50$  K in the 5H phase, and finally to an exchange-enhanced paramagnetic metal in the 6H phase, which may be close to a quantum critical point. (3) In the  $Ca_{1-x}Sr_xIrO_3$  system, high pressure stabilizes the post-perovskite structure on the Ca side ( $x < 0.3$ ), but favors the perovskite structure on the Sr side ( $x > 0.6$ ). Refs. J.-G. Cheng, *et al.* PRB **80**, 104430(2009); **80**, 174426 (2009); **81**, 134412(2010); JACS **131**, 7461(2009).

<sup>1</sup>Supported by NSF-DMR-0904282. Work under the supervision of Profs. J.-S. Zhou and J. B. Goodenough.