the unit cell), T-192 (tetragonal, with 190-192 atoms per unit cell), and γ-boron (high pressure phase, orthorhombic, with 28 atoms per unit cell). The new phase turned out to be a key to understanding the phase diagram of boron-the only element for which the phase diagram was unknown since its discovery 200 years ago.

Here, we report the synthesis of γ- and T-192 boron from β-boron at pressures up to 18 GPa and temperatures up to 2200 °C using a multianvil apparatus combined with x-ray diffraction (XRD) and Raman spectra. Based on the XRD and Raman results, we give the phase boundary of β-, γ-, and T-192 boron. Fig.1 shows the phase relations between β-boron (open), γ-boron (solid) and T phase (inverse triangles) based on the results of the multianvil quenched experiments. The semi-solid circles represent β-boron and γ-boron in coexistence. The line is a phase boundary between β-boron and γ-boron, and the inset show the theoretical phase boundary from Oganov *et al.*[1] and the tentative phase boundary from Zarechnaya *et al.*[2]. Additionally, the two open inverse triangle represent P-T conditions of T-192 phase from Oganov *et al.*[1] and Ma *et al.*[3] respectively. Combined with the previous results [1], [2] and our study, γ-boron phase becomes stable under a certain pressures (above ~8.5 GPa), and β-boron can transform into γ-boron above ~8.5 GPa and using heating to overcome kinetic barriers, and the kinetic barriers decrease with increasing pressure. However, at higher temperatures, β-boron and T-192 phase are more stable than γ-boron, thus γ-boron transforms back to β-boron (~9 GPa) or continues to transform into T-192 phase (above ~10 GPa) with increasing temperature depend on undergoing high pressure.

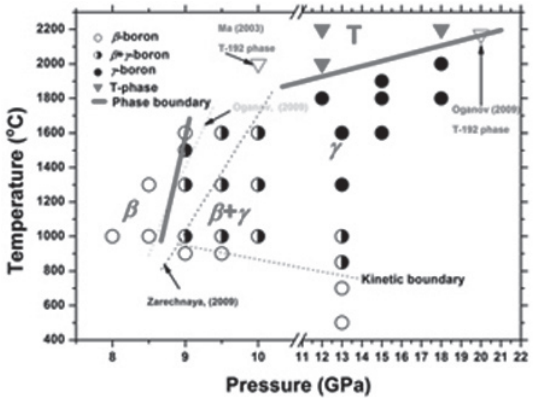

Fig.1 Phase relations between β-boron, γ-boron and T phase

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Structural anomaly in a novel iron-based perovskite

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Recent discovery of iron-based perovskites $ACu_3Fe_4O_{12}$ (A = Ca and La) has been attracting much interest due to the fascinating and unexpected properties. A charge disproportionation (CD) of Fe^{4+} into Fe^{3+} and Fe^{5+} occurs in $CaCu_3Fe_4O_{12}$ (CCFO) [1], whereas an intersite charge transfer (CT) between Cu and Fe results in a large volume change in $LaCu_3Fe_4O_{12}$ [2]. The different electronic phases resulted from CD/CT imply that further anomalous properties can be achieved in this system.

A novel iron-based perovskite $SrCu_3Fe_4O_{12}$ (SCFO) was successfully synthesized using high-pressure of 15 GPa. The structural and physical properties of SCFO were in contrast to those of the known $ACu_3Fe_4O_{12}$ (A = Ca and La) perovskites. SCFO demonstrated a large negative thermal expansion (NTE) with a linear expansion coefficient (ca. $-2x10^{-5}$ K^{-1} at maximum) in a temperature range of 170–270 K. The Rietveld refinement based on the synchrotron X-ray powder diffraction data revealed that the NTE was attributed to a continuous intersite CT between Cu and Fe. Mössbauer spectroscopy exhibited that SCFO resulted in a charge disproportionated state below ~200 K. The relative abundance of Fe^{3+}: Fe^{5+} = 4: 1, which is different from the ratio of 1: 1 for CCFO, implies the electron doping into Fe through intersite charge transfer.

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Keywords: novel perovskite, negative thermal expansion, high-pressure synthesis

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Electron and magnetic properties in high temperatures magnetic semiconductors at high pressure up to 7 GPa

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In high-temperature ferromagnetic semiconductors $Cd_{1-x}Mn_xGeAs$ (x=0÷0.36) and $Cd_{1-x}Mn_xGeP_2$ (x=0÷0.225) there is carried out a complex investigation of electric and magnetic properties. The baric dependences of the specific resistance ρ, Hall coefficient R_H, and relative magnetic susceptibility χ/χ_0 are measured. The ρ(P) and R(P) are measured in high-pressure device of "Toroid" type [1], [2] when pressure rises and falls up to 7 GPa. The magnetic susceptibility is estimated by a method described in the work [3]. Structural phase transitions are found in baric dependences of ρ(P) and R_H(P) in both compounds at increase and decrease in pressure. A position of phase transitions sifts towards the high pressures when a percentage of Mn increases. All phase transitions are reversible in $Cd_{1-x}Mn_xGeAs_2$, in $Cd_{1-x}Mn_xGeP_2$ samples with x≤0.135 the phase transition is accompanied by partial decomposition of a substance, what confirms the X-ray diffraction study before and after pressure applying on dependences (χ/χ_0)P. In all samples of both compounds there are observed the magnetic phase transitions which shift towards high pressures with increase in percentage of Mn. When pressure decreases the hysteresis emerges. A magnetic phase transition is not revealed in base samples of CdGeAs and CdGeP. We interpret the observed phase transitions as non-magnetic phase transition [4]. The temperature dependences of normal and abnormal Hall coefficients are calculated from magnetic-field dependences of Hall resistance for $Cd_{1-x}Mn_xGeAs_2$ (x=0÷0.36) by the method of interactive graphical plotting.