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Preparation and Thermoelectric Properties of *p*-Type Yb-Filled Skutterudites

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p-Type $Yb_zFe_{4-x}Co_xSb_{12}$ skutterudites were prepared by encapsulated melting and hot pressing, and the filling and doping (charge compensation) effects on the transport and thermoelectric properties were examined. The electrical conductivity of all specimens decreased slightly with increasing temperature, indicating that they were in a degenerate state due to high carrier concentrations of 10^{20} cm^{-3} to 10^{21} cm^{-3}. The Hall and Seebeck coefficients exhibited positive signs, indicating that the majority carriers are holes (*p*-type). The Seebeck coefficient increased with increasing temperature to maximum values of 100 μV/K to 150 μV/K at 823 K. The electrical and thermal conductivities were reduced by substitution of Co for Fe, which was responsible for the decreased carrier concentration. Overall, the Yb-filled Fe-rich skutterudites showed better thermoelectric performance than the Yb-filled Co-rich skutterudites.

Key words: Thermoelectric, skutterudite, ytterbium filling, charge compensation

INTRODUCTION

The rattling effect of filler atoms in thermoelectric materials with a skutterudite structure has been used to reduce the lattice thermal conductivity. The fillers (rattlers) scatter phonons, which reduces the phonon mean free path. This concept is one of the phonon-glass electron-crystal (PGEC) approaches proposed by Slack.[1] The fillers are located at the voids of the skutterudite lattice, loosely bonded with the host atoms, and can absorb heat through thermal vibrations.[2] Therefore, the filled skutterudite exhibits remarkably decreased thermal conductivity. Much research has examined the extent of the thermal conductivity reduction at a specific temperature in the filled skutterudite by controlling filler atoms, filling fraction, atomic displacement, and frequency.[3–9]

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The filled skutterudite is a superior thermoelectric material due to its high electrical conductivity and low lattice thermal conductivity. Recently, *n*-type filled skutterudites achieved high *ZT* values by single or double filling (*ZT* = 1.4), and triple filling (*ZT* = 1.7),[10–13] where *ZT* is the dimensionless figure of merit. However, *p*-type filled skutterudites have relatively low *ZT* values of less than 1.0.[3–7] Therefore, better *p*-type filled skutterudites that are compatible with *n*-type filled skutterudites need to be developed.

The filled skutterudite has the chemical formula RM_4X_{12}, where R is an alkaline, alkaline-earth, or rare-earth element, M is Fe, Ru, Os, Co, Rh or Ir, and X is P, As or Sb. Research on filled skutterudites has focused on RCo_4Sb_{12}-based materials for *n*-type and RFe_4Sb_{12}-based materials for *p*-type. The rare-earth-filled RFe_4Sb_{12} skutterudites form a very important group amongst the *p*-type skutterudites, and many interesting physical characteristics have been reported.[14] The RFe_4Sb_{12} skutterudites