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Crystal Structure and Thermoelectric Properties of Misfit-Layered Sulfides $[Ln_2S_2]_pNbS_2$ (Ln = Lanthanides)

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Polycrystalline samples of misfit-layered sulfides $[Ln_2S_2]_pNbS_2$ (Ln = lanthanides) have been prepared using the CS_2 sulfidation method. Except for Ln = Eu and Lu, single-phase samples were prepared. The compounds consist of an alternate stacking of a trigonal prism-type $[NbS_2]$ layer and a double-layered NaCl [rock salt (RS)]-type $[Ln_2S_2]$ block, parallel to the *c*-axis. Three types of stacking modes of the $[NbS_2]$ layer and the RS-type block have been confirmed with a (3 + 1)-dimensional superspace group description: two face-centered orthorhombic structures and one face-centered monoclinic structure. Slightly cation-deficient samples with Ln = Yb exhibit the highest Seebeck coefficient $S \approx 59\ \mu$V/K. With electrical resistivity of $\rho = 1.4\ m\Omega$ cm and thermal conductivity of $\kappa = 0.69$ W/Km, this yields a dimensionless figure of merit of $ZT = 0.11$ at 300 K.

Key words: Misfit-layered sulfides, superspace group, structure modulation, thermoelectric properties

INTRODUCTION

Since the discovery of the superb thermoelectric (TE) properties in $[Ca_2CoO_3]_pCoO_2$,[1–3] misfit-layered (ML) compounds have attracted considerable interest as potential TE materials. For a good TE material, high TE power factor (S^2/ρ, S: Seebeck coefficient; ρ: electrical resistivity) and low lattice thermal conductivity, κ_L, are required, but such a situation is hard to realize in conventional compounds due to the correlation between these parameters. Since ML compounds consist of mutually incommensurate subsystems, positional modulation of the constituent atoms is usually observed and such modulation can effectively reduce κ_L. If we can appropriately design one subsystem as a good electrical conductor with little modulation while the other subsystem is a poor thermal conductor with significant modulation, the resulting tailored multilayer structure will exhibit good TE properties.

Imai et al.[4] first investigated the TE properties of a single-crystalline ML $[Sn_2S_2]_pTiS_2$ sample and reported that the sample exhibits a reasonable value of $S^2/\rho = 6 \times 10^{-4}$ W/K^{2}m to 12×10^{-4} W/K^{2}m at 300 K. Because titanium sulfide is an *n*-type material, a corresponding *p*-type material with excellent TE properties is required for designing a TE device. Miyazaki et al.[5,6] then reported a preliminary study on the TE properties of $[Ln_2S_2]_pNbS_2$ (Ln = lanthanides). Wan et al.[7] studied the high-temperature TE properties of $(SnS)_{1.2}(TiS_2)_2$ and reported that its ZT exceeds 0.35 at 670 K. Quite recently, Cr-based ML sulfides have also been prepared and their TE properties measured.[8] However, the crystal structure and Ln-dependent TE properties have not been fully investigated. In this study, we present the symmetry, lattice parameters, and TE properties of a series of $[Ln_2S_2]_pNbS_2$ samples.

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EXPERIMENTAL PROCEDURES

Polycrystalline samples were prepared from lanthanide oxides (99.9% or higher) and Nb_2O_5 (99.9%) reagents. Appropriate amounts of the powder mixture were pressed into pellets and then heated on a quartz boat at 1050°C for 12 h in flowing mixed gas of CS_2 and Ar, which was obtained by bubbling Ar