Catalyst-assisted growth of MB₆ (M=Sr, Ba) 1D nanostructures was achieved by pyrolysis of B₂H₆ over alkaline-earth metal oxide (MO) or alkaline-earth metal carbonate (MCO₃) powders at elevated temperature (~890-960 ºC) and low pressure (~165 mTorr). Ni, Au and Pd are effective catalytic materials. Results show that the MB₆ nanostructures are several tens of nanometer in diameter and up to ten micrometer in length (Fig. a). The MB₆ nanostructures are single crystalline with preferred growth direction along [001] (Fig. b). For most of nanostructures, there is an amorphous oxide layer surrounding the crystalline core structure (Figs. b and c) The growth of these MB₆ nanostructures involved both vapor-liquid-solid and vapor-solid growth mechanisms. The MB₆ 1D nanostructures are appealing candidates for high temperature thermoelectric energy conversion.