YTTRIUM INSERTION INTO THE $CoSb_3$ SKUTTERUDITE BY HOT-PRESSED METHOD

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Abstract: The yttrium filling skutterudite compound was prepared by hot-pressed method under pressure of 30MPa. It was found that yttrium atoms could be inserted in the vacant site of the $CoSb_3$ skutterudite. The crystal structure of resulting $Y_xCo_4Sb_{12}$ (x = 0 ÷ 0.15) was refined by the Rietveld refinement of the X-ray diffraction data.

1. Introduction

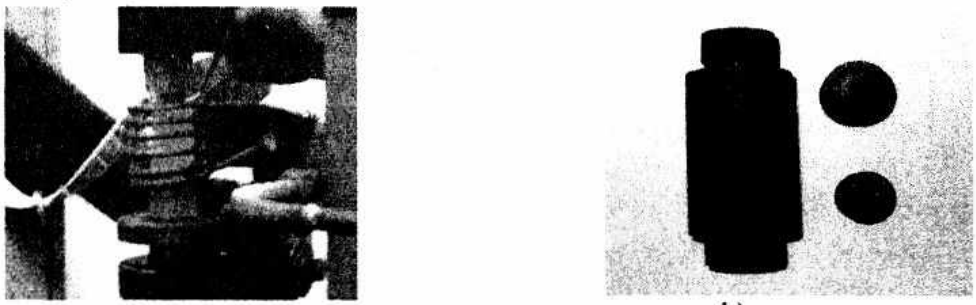
Skutterudite-type structure is a cubic structure with the space group Im-3 composed of eight corner-shared MX_6 octahedra (M=Co, Fe, Ru, Os; X = P, As, Sb). The structure is closely related to the perovskite-type structure. The linked octahedra produces a void at the center of $(MX_6)_8$ – cluster and this void (vacant site) occupies a body-centered position of the cubic lattice. This void is large enough to accommodate large metal atoms, resulting in the formation of filled- skutterudite structures with the general formula RM_4X_{12} (Sn, Ce, Pr)[1]. Recently, these compounds are highlighted as thermoelectric conversion materials with high conversion efficiency. Generally, these compounds show very high carrier mobilities and large thermoelectric power. If lowering the thermal conductivity of the skutterudites compounds with a minimal reduction in the electrical properties can be achieved, high ZT values might be possible. In the filled skutterudites compounds, loosely bound R atoms have unusually large thermal vibration amplitudes. Consequently, remarkable reduce in thermal conductivity is expected by strong phonon scattering [2].

In previous study [3], we have synthesized the filling skutterudite $Y_xCo_4Sb_{12}$ compounds by inductive melting followed by sintering in vacuum and have investigated the solubility limit of Y on these compounds. In this study, yttrium atom insertion in the $CoSb_3$ lattice has been performed under hot-pressed conditions. We have investigated the structural of the general form $Y_xCo_4Sb_{12}$ (x=0-0.15). The Rietveld refinement method was used for refining structure parameters and for examining yttrium distribution in $CoSb_3$ structure.

2. Experimental

Sb (99.9999% pure),Y (99.9% pure) shots and Co (99.99% pure) powder were used as starting materials. Polycrystalline $CoSb_3$ ingots were prepared as follows. Stoichiometric mixture of cobalt and antimony (Co:Sb = 1:3) was loaded into quartz ampoules. These ampoules were sealed under vacuum 10^{-5} mmHg. They were heated in a furnace at 600°C for 24 h and quenched to room temperature.

Yttrium atom insertion in the $CoSb_3$ host lattice was done by two steps: the first - preparing Y_3Co_2 powder by direct reaction from the cobalt and yttrium liquid in inductive furnace, the second step - reaction from the $CoSb_3$ and Y_3Co_2 powder by hot-pressed method (Fig.1a). Powder of Y_2Co_3 was mixed with $CoSb_3$ powder in the molar ratio corresponding to the stoichiometric filled skutterudite composition $Y_xCo_4Sb_{12}$ (x=0, 0.025, 0.05, 0.075, 0.10, 0.15). The mixed powder was ground and put into a cylindrical graphite mould (Fig.1b). The reactions were carried out at pressure of 30 MPa using a conventional hot-press. The reaction temperature and the duration were fixed to 650°C and 15 min.



a) b)

Fig.1. The conventional hot-press (a) and the cylindrical graphite mould (b)

3. Results and discussion

Single-phase $CoSb_3$ with the cubic skutterudite-type structure was obtained. The lattice parameter was determined to be a=9.028 A°, which was in good agreement with previous studies [3,5]. Figure 2 shows the surface micrograph of $CoSb_3$ sample. EDS analysis of this image (Fig.3- curve1) show that cobalt concentration of the particles was not changed. The reaction of cobalt particles and antimony liquid was completed. The curve 2 on the fig.3 shows the EDS spectrum of the filled skutterudite $Y_xCo_4Sb_{12}$ (x=0.15).

In previous study [3], we have synthesized the filling skutterudite $Y_xCo_4Sb_{12}$ compounds by inductive melting followed by sintering in vacuum at 1030°C and found that second-phase SbY was formed. In this study, the reaction temperature was fix to 650°C because the host material decomposed to arsenopyrite-type $CoSb_2$ and Co at higher temperature. The XRD analysis of these samples (Fig.4- curves a) show that SbY phase was not formed under hot-pressed conditions. The lattice parameter increases with increasing Y filling fraction x. Depend the values of x, the lattice parameter was increased in the range from 9.0279 A° to 9.0385 A°. The increase of the lattice parameter was explained by the formation of filled skutterudite $Y_xCo_4Sb_{12}$ or the position of antimony atoms were replaced by yttrium atoms. The Rietveld refinement method was used for refining the structure parameters (lattice parameter *a*, Y atoms positions) and for analyzing the Y atom site distribution in the $CoSb_3$ structure. The initial input parameters for the cobalt and antimony positions were assumed to be the same as those obtained for the arsenic positions in the isotype compound – $CoAs_3$ (space group: Im-3). The resulting parameters obtained for undoped $CoSb_3$ were used in the analysis of yttrium distribution in the $CoSb_3$ structure. Two alternative models of Y-doped $CoSb_3$ structure were considered: A (Fig.4-curve b): Y substitutes Sb in the 24*g* (0,y,z) site or B (Fig.4-curve c): Y fills the voids in the 2*a* (0,0,0) site. Both the models were refined using XRD patterns for the sample x=0.075.

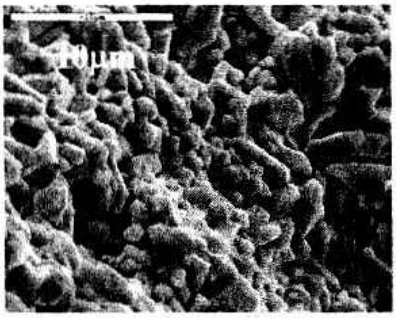


Fig.2. Surface micrograph (SEM) of the sample $Y_{0.15}Co_4Sb_{12}$

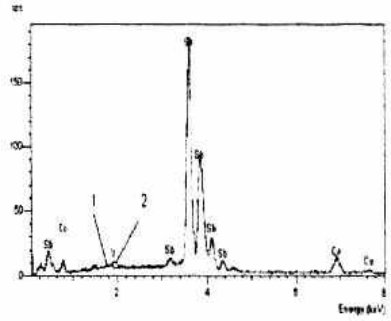


Fig.3. EDS-Spectra on the sample $CoSb_3$ (curve1) and the sample $Y_{0.15}Co_4Sb_{12}$ (curve 2)

The refinement by RIETAN 2000 program [4] was carried out for 52 reflections. Analysis of the calculated patterns show that filling the void with Y in the 2*a* site leads to extinction of low-angle reflections (011), (002), (112). Thus, it can be stated that model B fits experimental data considerably better then model A. The statistic parameters such as a goodness-of-fit (S) were 2.47 and 1.85 for the model A and model B, respectively. In conclusion, it can be assumed that Y atoms fills the voids in the skutterudite structure.

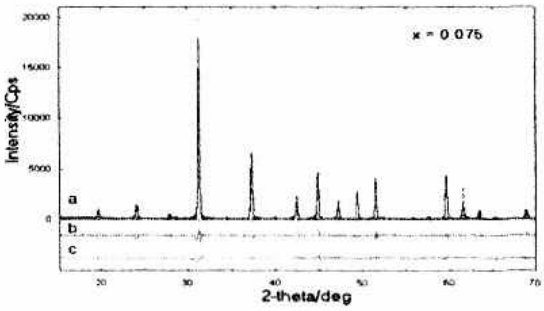


Fig.4. XRD pattern of the sample x=0.075: (a) the solid points are the experimental data, while solid line represents a fitting with Rietveld methode,(b,c) differential line for model A and B, respectively

4. Conclusions

Polycrystalline samples of $CoSb_3$ skutterudite compounds were prepared by melting the appropriate quantities of component elements. Yttrium atom insertion in the $CoSb_3$ lattice has been performed under hot-pressed method. We have investigated the structural of the general form $Y_xCo_4Sb_{12}$ (x=0 - 0.15). SbY phase was not formed under hot-pressed conditions. The Rietveld refinement method was confirmed that Y atoms fills the voids in the skutterudite structure.

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