Effects of Doping on Boride Thermoelectrics

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Introduction:

Approximately two thirds of the primary energy consumed by mankind is lost, with much of the loss being in the form of waste heat. Thermoelectrics can be used to recover some of that energy by converting a temperature gradient into an electrical current [1]. An ideal thermoelectric has a high Seebeck coefficient, which means it can produce many volts of potential per temperature change across the material, a low electrical resistivity, allowing for easy electronic transport across the material, and a low thermal conductivity, allowing for a temperature gradient to more easily be created across the material. The product of the Seebeck coefficient squared and electrical resistivity are referred to as a material's power factor, which is a measure of how much electrical power the thermoelectric can produce.

Thermoelectrics can be either p-type or n-type depending on whether the material's charge carriers are holes or electrons. Having matching p- and n-type thermoelectrics increases device efficiency. Borides, an attractive candidate for high temperature thermoelectrics, are mostly p-type due to a two electron deficiency in the boron icosahedra in their crystal structure [2]. However, by adding metals such as aluminum to yttrium boride (YB_{25}), one can add electrons to the valence band of the boride, transitioning the thermoelectric into n-type [3]. Doping with vanadium has been shown to improve the thermoelectric properties of another n-type boride, $YB_{22}C_2N$ [4]. In this report, vanadium (V) and manganese (Mn) were doped into yttrium aluminum boride ($YAlB_{14}$) in an attempt to add electrons to the boride valence band, improving the thermoelectric properties of the material.

Methods:

Yttrium oxide and boron powder were mixed together in a 3:8 weight ratio and heated under vacuum at 1600°C for eight hours to make YB_{25}. Samples were ground and washed in 33% nitric acid to remove impurity phases. The powder was rinsed in water, ethanol and acetone and dried. Al powder was added to the powder in a 2:1 YB_{25} to Al weight ratio. The mixture was held at 1300°C for four hours to form $Y_{0.6}Al_{0.6}B_{14}$. The pellet was ground and washed in a sodium hydroxide solution overnight to dissolve any remaining aluminum. The powder was rinsed in water ethanol and acetone.

For the V-doped sample, $Y_{0.6}Al_{0.6}B_{14}$ (0.762g) and vanadium diboride (0.042g) were heated to 1500°C for five minutes at 100 MPa using a spark plasma sintering system. The Mn-doped sample was made by adding $Y_{0.6}Al_{0.6}B_{14}$ (0.770) and manganese powder (0.036g) and heating in the same manner. Undoped $Y_{0.6}Al_{0.6}B_{14}$ pellet was made by heating the powder (0.84g) under the same conditions in the spark plasma sintering system. Seebeck coefficient and resistivity measurements were made using ZEM-2. Annealed samples were made by annealing at 1000°C for eight hours under vacuum and four hours under argon, respectively.

Results:

Doping YAlB with V and Mn improved the thermoelectric properties. Resistivity for both samples was much lower than for the undoped sample as shown in Figure 1. Both V and Mn are capable of donating some electrons to the boride electrical network. The addition of carriers to the conductive network increases the conductivity of the material. Unfortunately it also lowers the Seebeck coefficient as seen in Figure 2, as the voltage produced by a temperature difference is lower upon the addition of more carriers. However, by combining the two factors, one can see that the power factor for doping with both elements is larger than that of the undoped sample.

To further improve the power factor, the V-doped sample was annealed both under vacuum and argon. When annealed under vacuum, the Seebeck coefficient improved, suggesting removal of dopants from the material. The resistivity did not change with annealing, suggesting the removal of impurities from the material and the resulting decrease in resistivity balanced out the increase in resistivity caused by the removal of dopants. When the sample was annealed under argon, the Seebeck coefficient and resistivity both decreased, which is consistent with an increase in doping, as the extended heating assumedly allowed the vanadium to intercalate into the structure. The power factor for both annealing processes was higher than for the un-annealed sample. The sample annealed under vacuum had the highest power factor.

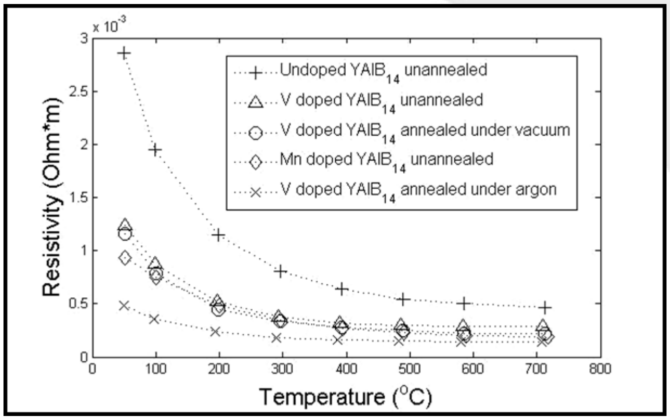

Figure 1: Resistivity of vanadium and manganese doped samples. Most samples had similar resistivities. Undoped $YAlB_{14}$ had high resistivity, and vanadium doped $YAlB_{14}$ annealed under argon had low resistivity.

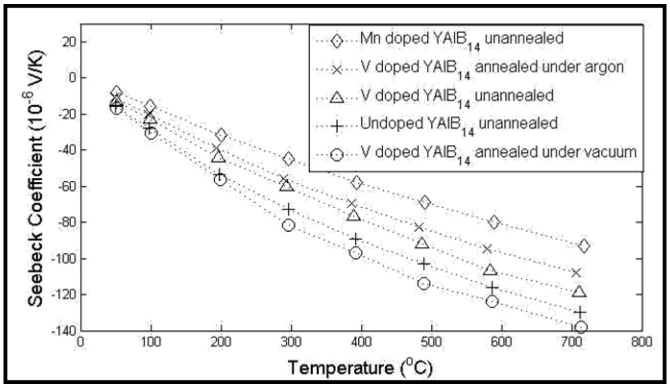

Figure 2: The Seebeck coefficient of vanadium and manganese doped samples. The lowest Seebeck coefficient belongs to manganese doped $YAlB_{14}$, and the highest is vanadium doped $YAlB_{14}$ annealed under vacuum.

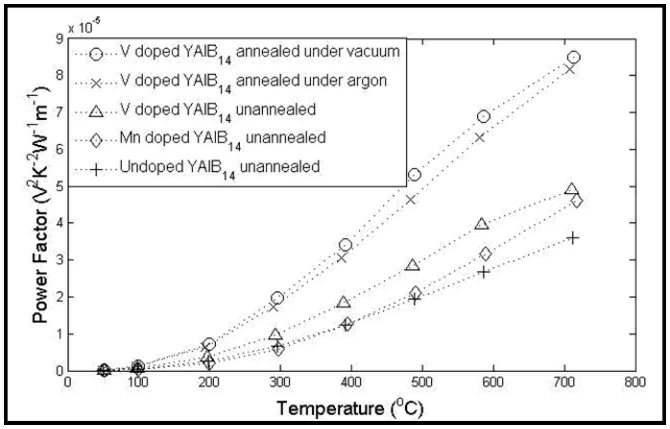

Figure 3: Power factor of vanadium and manganese doped samples. Annealed vanadium doped samples had the highest power factor.

Conclusions:

Yttrium aluminum bromide's thermoelectric properties can be enhanced by additional doping with vanadium and manganese as well as annealing the sample after doping. However the thermoelectric properties are still much poorer than the p-type boron carbide. Further research is needed to determine which dopants increase thermoelectric properties, and to discover the mechanism by which annealing changes the Seebeck coefficient. This will lead to a better understanding of how to create more efficient n-type boride thermoelectrics.

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