RMn₂Si₂ (R = La, Ce, Pr, Nd, Sm, Gd) Compounds Grown from Metal Flux and Properties of the Crystals

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金属フラックスから RMn₂Si₂ (R = La, Ce, Pr, Nd, Sm, Gd) 化合物の育成と結晶の性質

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RMn₂Si₂ (tetragonal, S.G.: *I4/mmm*) (R = La, Ce, Pr, Nd, Sm and Gd) crystals were grown from high-temperature lead metal flux by slowly cooling under an argon atmosphere. The RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) crystals were obtained as thin plates with well-developed {001} faces. The largest crystals have maximum dimensions of approximately 2.3 × 2.3 × 0.02 mm³. LaMn₂Si₂ was generally obtained as a powder of irregular shape. The values of the micro-Vickers hardness for the {001} faces of RMn₂Si₂ are in the range of 5.8 ± 0.4 to 6.5 ± 0.5 GPa. The oxidation process of RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) crystals was studied at the temperature below 1473 K by thermogravimetric and differential thermal analyses (TG-DTA). The TG curves show that the oxidations of CeMn₂Si₂, PrMn₂Si₂, NdMn₂Si₂, SmMn₂Si₂, GdMn₂Si₂ crystals start at approximately 738, 979, 999, 784, and 763 K, respectively. The weight gains of the compounds after TG determination were measured to be in the range of 16.4 to 29.2 mass%. The results of magnetic susceptibility measurements agree with recent previous studies on these compounds.

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Key-words : RMn₂Si₂ (R = Ce, Pr, Nd, Sm, Gd) crystal, Unit cell parameters, Hardness, Thermal stability, Magnetic susceptibility

1. Introduction

RMn₂Si₂ (tetragonal, S.G.: *I4/mmm*) single crystals have attracted considerable interest because of their remarkable properties and potential application as high-temperature thermoelectrics.¹⁾ However, the data available on the properties of RMn₂Si₂ are in most cases obtained from measurements of polycrystalline samples. Therefore, it is desirable to grow single crystals, to obtain more reliable information on the properties. Ternary rare earth manganese silicides have been synthesized by the solid-state reaction method,¹⁾ arc-melting method²⁾ and molten metal flux.³⁾⁻⁵⁾ In this study, we report the experimental conditions for growing relatively large single crystals of RMn₂Si₂ (R = La, Ce, Pr, Nd, Sm and Gd) from a high-temperature lead flux in an argon atmosphere. La, Ce, Pr, Nd, Sm and Gd are selected as rare earth elements from the light and middle region of the lanthanide series.

These compounds were characterized by micro-Vickers hardness, oxidation resistance heated in air and magnetic susceptibility at low temperatures.

2. Experimental

2.1 Syntheses of crystals

The reagents used to prepare the samples were small pieces of 99.9% rare earth elements (La-Gd), 99.9–99.99% Mn

pieces, 99.99% Si powder and 99.99% Pb pieces. The rare earth elements (R = La, Ce, Pr, Nd, Sm and Gd), Mn and Si were mixed together at atomic ratios of R : Mn : Si = 1 : 2 : 2. The amount of Si in the starting materials was fixed at 0.4 g throughout all the experiments. Lead was added to these mixtures at a ratio of 3.8 : 1 in weight. The mixture of starting materials was placed in a high purity (99.9%) hBN crucible (20 mm diameter and 30 mm length) together with a hBN cover and heated in an Ar atmosphere at 1623 K for 5 h. The solution was cooled to 1073 K at a rate of 50 K h⁻¹ and then quenched to room temperature. Dissolving the lead in a solution of dilute acetic acid separated the crystals.

2.2 Characterization

The crystal structures and unit cell parameters of the phases were examined by X-ray diffraction (XRD) with monochromatic Cu Kα₁ radiation. Relatively large crystals of RMn₂Si₂ were selected under a stereomicroscope. The morphology of the crystals was examined using a four-circle diffractometer and scanning electron microscopy (SEM). The chemical composition and impurity of the crystals were analyzed with an electron probe microanalyzer (EPMA) and an energy-dispersive detector (EDX).

The micro-Vickers hardness for the crystals was measured at room temperature in air. A load of 0.49 N was applied for

15 s at approximately four positions on a well-developed {001} plane of each crystal. The obtained values were averaged and the experimental error was estimated.

The oxidation resistance of RMn₂Si₂ crystals was studied by thermogravimetric and differential thermal analyses (TG-DTA).^{5,6} Pulverized samples of approximately 20 mg were heated at a rate of 10 K min⁻¹ in air.

Magnetic susceptibility of the powder samples of RMn₂Si₂ was measured using a commercial superconducting quantum interference device (SQUID) magnetometer in the temperature range of 2 K to 300 K.

3. Results and discussion

The XRD evidence for the crystalline phases of RMn₂Si₂ obtained after reaction is shown **Fig. 1**. As seen from **Fig. 1**, for the La-Mn-Si system, LaMn₂Si₂, MnSi, Mn₅Si₃ and an unknown phase were obtained, for the Ce-Mn-Si system, CeMn₂Si₂, MnSi and an unknown phase were obtained, for the Pr-Mn-Si system, PrMn₂Si₂ and Mn₅Si₃ were obtained, for the Nd-Mn-Si and Sm-Mn-Si systems, NdMn₂Si₂ or SmMn₂Si₂, Mn₅Si₃ and an unknown phase were obtained, and for the Gd-Mn-Si system, only GdMn₂Si₂ was obtained, while crystals of RMnSi (TiNiSi- and PbFCl-type structures) and R₂Mn₃Si₅ (Sc₂Fe₃Si₅-type structure)¹⁾ were not detected by XRD. The RMn₂Si₂ single crystals, having a silver-gray and metallic luster, were generally obtained in the form of thin plates with well-developed {001} faces as shown in **Fig. 2** (NdMn₂Si₂). The largest crystals have maximum dimensions of approximately 2.3 × 2.3 × 0.02 mm³. However, LaMn₂Si₂ was generally obtained as powder of irregular shape.

The basic crystal data and chemical compositions of RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) are listed in **Table 1**. The unit cell parameters of RMn₂Si₂ crystals are in relatively

good agreement with previously published data ($a = 0.4010(5)$ nm and $c = 1.0523(5)$ nm for CeMn₂Si₂; $a = 0.4025$ nm and $c = 1.0555$ nm for PrMn₂Si₂; $a = 0.40155(5)$ nm and $c = 1.0542(5)$ nm and $a = 0.4011$ nm and $c = 1.0552$ nm for NdMn₂Si₂; $a = 0.3975$ nm and $c = 1.0520$ nm for SmMn₂Si₂; $a = 0.3950$ nm and $c = 1.0478$ for GdMn₂Si₂).⁷⁾ The EDX results show that RMn₂Si₂ compounds have homogeneity ranges. No evidence has been obtained for the presence of a lead-containing phase in the crystals as concluded from the EPMA and EDX of RMn₂Si₂ crystals.

The microhardness values of CeMn₂Si₂, PrMn₂Si₂, NdMn₂Si₂, SmMn₂Si₂ and GdMn₂Si₂ are 5.8 ± 0.6 , 6.5 ± 0.5 , 6.3 ± 0.4 , 6.5 ± 0.4 and 6.8 ± 0.2 GPa, respectively. The microhardness values of RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) crystals have not been reported in the earlier literature. These values of RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) are found to be very similar to previously published data for RMn₂Si₂ (R = Er, Tm, Yb, Lu and Y) observed in the range of 5.0 ± 0.4 – 7.9 ± 0.3 GPa.^{5,6)}

The oxidation process of RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) crystals was studied below 1473 K by TG-DTA analyses, as shown in **Fig. 3**.

Fig. 2. SEM micrograph of NdMn₂Si₂ crystal.

Fig. 1. Powder XRD patterns of the products obtained from R-Mn-Si (R = La, Ce, Pr, Nd, Sm and Gd) systems.
○ RMn₂Si₂, ● MnSi, △ Mn₅Si₃, × unknown.

Fig. 3. TG-DTA curves of RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) crystals heated in air.

Table 1. Results of the Unit Cell Parameters and Chemical Analyses for RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) Crystals

Formula unit	CeMn ₂ Si ₂	PrMn ₂ Si ₂	NdMn ₂ Si ₂	SmMn ₂ Si ₂	GdMn ₂ Si ₂
Crystal	plate	plate	plate	plate	plate
<i>a</i> (nm)	0.4009(1)	0.4029(1)	0.4008(1)	0.3973(1)	0.3947(1)
<i>c</i> (nm)	1.0519(1)	1.0557(1)	1.0542(1)	1.0510(1)	1.0470(1)
<i>V</i> (nm ³)	0.1691(1)	0.1714(1)	0.1693(1)	0.1659(1)	0.1631(1)
R (mass%)*	44.4	44.7	45.2	47.2	47.8
Mn (mass%)*	37.4	37.4	36.3	35.1	33.6
Si (mass%)*	18.2	17.9	18.5	17.7	18.6
Chemical composition	Ce _{1.0} Mn _{2.1} Si ₂	Pr _{1.0} Mn _{2.1} Si ₂	Nd _{0.9} Mn _{2.0} Si ₂	Sm _{1.0} Mn _{2.0} Si ₂	Gd _{0.9} Mn _{1.9} Si ₂
*EDX results					
Crystal structure : tetragonal, space group I4/mmm, formula units per unit cell Z=2					

Table 2. Results of the TG/DTA Measurements for RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) Compounds

Compound	Oxidation start (K)	Exothermic maximum (K)	Weight gain (mass%)	Oxidation products
CeMn ₂ Si ₂	738	1117, 1184, 1322, 1431	29.2	Ce ₄ Si ₃ O ₁₂ , MnSiO ₃ , Ce ₂ O ₃ , Mn ₅ Si ₃ , unknown
PrMn ₂ Si ₂	979	1200, 1305, 1366, 1444	26.8	Pr ₄ Si ₃ O ₁₂ , MnSiO ₃ , Mn ₅ Si ₃ , unknown
NdMn ₂ Si ₂	999	1218, 1335, 1392	16.4	Nd ₄ Si ₃ O ₁₂ , Mn ₅ Si ₃ , MnSiO ₃ , unknown
SmMn ₂ Si ₂	784	1333, 1408, 1453	19.6	Sm ₄ Si ₃ O ₁₂ , MnSiO ₃ , Mn ₅ Si ₃ , Sm ₂ O ₃
GdMn ₂ Si ₂	763	1213, 1270, 1402	23.9	Gd ₄ Si ₃ O ₁₂ , Gd ₂ O ₃ , unknown

The oxidation of CeMn₂Si₂, PrMn₂Si₂, NdMn₂Si₂, SmMn₂Si₂ and GdMn₂Si₂ crystals began to proceed at approximately 738, 979, 999, 784 and 763 K, respectively. The weight gain of the compounds after heating in air up to 1473 K was 29.2, 26.8, 16.4, 19.6 and 23.9 mass%, respectively. CeMn₂Si₂ had a low oxidation resistance, while NdMn₂Si₂ had a relatively high oxidation resistance. The final oxidation products were R₄Si₃O₁₂ (R = Ce, Pr, Nd, Sm and Gd), R₂O₃ (R = Ce, Sm and Gd), MnSiO₃, Mn₅Si₃⁸⁾ and an unknown phase, and so the exothermic peaks are attributed to oxidation products. The results of TG-DTA are listed in Table 2.

Magnetic characterization of the RMn₂Si₂ (R = Ce, Pr, Nd, Sm and Gd) samples was carried out by measuring the magnetic susceptibilities. Our results agree with recent previous work which has been done on these compounds.⁹⁾⁻¹¹⁾

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