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A study on the formation of $ThMn_{12}$ and $NaZn_{13}$ structures in $RFe_{10}Si_2$

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Abstract

$RFe_{10}Si_2$ (R≡La, Pr, Nd, Sm, Gd, Er and Zr) compounds were synthesized by the rapid quench method. The $ThMn_{12}$ structure can be obtained in the $RFe_{10}Si_2$ system containing R≡Sm, Gd and Er, while the $NaZn_{13}$ structure can be obtained in the system containing R≡La, Pr and Nd. It has also been found that $Nd_{1-x}Zr_xFe_{10}Si_2$ ($x=0.25$, 0.5 and 0.75) crystallized in the $ThMn_{12}$ structure. The factors which control the formation of $ThMn_{12}$ and $NaZn_{13}$ structures in the $RFe_{10}Si_2$ system are discussed with respect to the atomic radius of the rare earth site element.

Iron-rich rare earth intermetallic compounds have attracted much interest as novel permanent magnet materials since the discovery of Nd–Fe–B magnets in 1983 [1]. In a rare earth (R) and 3d transition metal (M) binary system, RM_{13} and RM_{12} have already been known as M-rich compounds. RM_{13} crystallizes in a $NaZn_{13}$-type cubic structure and RM_{12} in a $ThMn_{12}$-type tetragonal structure. In particular, interest has been focused on the latter system as a potential candidate for new-type permanent magnets, and their magnetic properties have been extensively studied. In binary systems, however, the $ThMn_{12}$ structure exists only for M ≡ Mn. For the iron-containing compound, this crystal structure can be obtained in a pseudo-binary system $RFe_{12-x}T_x$ (T≡Al, Si, Ga, Ti, V, Cr, Mn, Mo, W and Re) [2–6]. On the contrary, the $NaZn_{13}$ structure exists only for M≡Co and Be in a binary system, and for the iron-containing compound, in a pseudo-binary system $RFe_{13-x}T_x$ (T≡Al, Si) [7, 8]. For T≡Si, both the iron-rich $ThMn_{12}$ and the iron-rich $NaZn_{13}$ structures can be obtained in the $RFe_{12-x}T_x$ and $RFe_{13-x}T_x$ systems respectively. Details of their structural behaviour, however, have not been investigated systematically.

The aim of the present investigation was to study the factors which control the formation of $ThMn_{12}$ and $NaZn_{13}$ crystal structures in the $RFe_{10}Si_2$ system using the rapid quench method.

Ingots of $RFe_{10}Si_2$ (R≡La, Pr, Nd, Sm, Gd, Er and Zr) were prepared by arc melting under a purified argon gas atmosphere from starting materials

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with at least 99.9% purity. Rapidly quenched ribbons were obtained from these ingots using the standard equipment for melt spinning with a copper roll (300 mm in diameter) under a purified argon gas atmosphere. The quenching rate was varied by changing the roll velocity V_r in the range 10–30 m s^{-1}. The crystal structures of these ribbons were determined by X-ray diffraction using Cu Kα radiation.

The rare earth dependence of the observed phase of $RFe_{10}Si_2$ (R ≡ La, Pr, Nd, Sm, Gd and Er) rapidly quenched samples is shown in Fig. 1. In Fig. 1, the X-ray main peak intensity ratio of phases observed in the samples plotted against the atomic radius of the rare earth. In the case of $V_r = 10$ m s^{-1}, the $ThMn_{12}$ phase was observed in the $RFe_{10}Si_2$ system containing R ≡ Sm, Gd and Er, while the $NaZn_{13}$ phase was observed in the system containing R ≡ La, Pr and Nd. The amounts of $ThMn_{12}$ and $NaZn_{13}$ phases increased with increasing V_r, e.g. for $V_r = 30$ m s^{-1} compared with $V_r = 10$ m s^{-1}, and the $ThMn_{12}$ phase was found in the $NdFe_{10}Si_2$ compound. This result indicates that a higher quenching rate induces the formation of iron-rich phases such as the $ThMn_{12}$ and $NaZn_{13}$ phases. The results shown in Fig. 1 also suggest that the atomic radius of rare earth elements is important in determining the crystal structure of iron-rich compounds, and that $NdFe_{10}Si_2$ is the boundary between the $ThMn_{12}$ and $NaZn_{13}$ phases [9, 10].

These results presumably reflect the fact that the free energy of the $ThMn_{12}$ and $NaZn_{13}$ phases may be sensitive to the Fe–Fe distance.

A large rare earth atomic radius should cause expansion of the Fe–Fe distance and stabilize the $NaZn_{13}$ phase which has more coordinated iron around R than the $ThMn_{12}$ phase has. On the contrary, the $ThMn_{12}$ phase may be more likely to occur than $NaZn_{13}$ in compounds which have a small rare earth atomic radius.

Next, attention was paid to the rare earth atomic radius effect. We focused on $NdFe_{10}Si_2$ (the atomic radius of neodymium is 1.82 Å) and investigated the $La_{0.5}Nd_{0.5}Fe_{10}Si_2$ and $Nd_{0.5}Er_{0.5}Fe_{10}Si_2$ compounds in which half of the neodymium atoms are replaced by lanthanum atoms (the atomic radius is 1.87 Å) and erbium atoms (the atomic radius is 1.75 Å) respectively in $NdFe_{10}Si_2$. The aim of this investigation was to control the phase which appeared by changing the average rare earth atomic radius. The $NaZn_{13}$

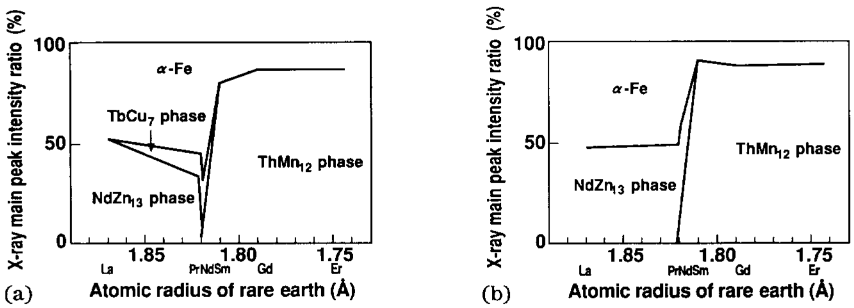


Fig. 1. Phases in rapidly quenched $RFe_{10}Si_2$: (a) $V_r = 10$ m s^{-1}; (b) $V_r = 30$ m s^{-1}.

phase was found in the $La_{0.5}Nd_{0.5}Fe_{10}Si_2$ compound ($V_r = 10$ m s^{-1}), and its lattice constant was 11.43 Å.

This value for the $NaZn_{13}$ phase is about the midvalue of the lattice constant of $LaFe_{10}Si_2$ and $NdFe_{10}Si_2$.

On the contrary, the $ThMn_{12}$ phase was found in the $Nd_{0.5}Er_{0.5}Fe_{10}Si_2$ compound ($V_r = 10$ m s^{-1}), and the lattice constants *a* and *c* were 8.420 Å and 4.744 Å respectively. These values for the $ThMn_{12}$ phase are about the midvalues between the lattice constants of $NdFe_{10}Si_2$ ($V_r = 30$ m s^{-1}) and $ErFe_{10}Si_2$ and are consistent with the values envisaged from the rare earth contraction of the $ThMn_{12}$ phase (Fig. 2).

The results show that the mean rare earth atomic radius of $RFe_{10}Si_2$ compounds are dominant in determining the crystal structure. Therefore it is possible to control the phase which appears by changing the average rare earth atomic radius.

We then investigated the (Nd, Zr)$Fe_{10}Si_2$ system in order to extend the above-mentioned atomic radius effect to the non-rare-earth element zirconium.

The atomic radius of zirconium is 1.60 Å and is smaller than that of erbium [9, 10]. The phases appearing in (Nd, Zr)$Fe_{10}Si_2$ ribbons ($V_r = 10$ m s^{-1}) are shown in Fig. 3, and their typical X-ray diffraction patterns are shown in Fig. 4. As seen in Fig. 3 and Fig. 4, a partial replacement of neodymium by zirconium drastically induced the formation of the $ThMn_{12}$ phase.

The measured lattice constant of these $ThMn_{12}$ phases are shown in Fig. 5. Both of the lattice constants *a* and *c* decrease linearly, depending on the mean atomic radius of neodymium and zirconium averaged by considering their contents. These values are on the line of rare earth contraction given in Fig. 2. The result indicates that even a non-rare earth element, zirconium, almost occupies the neodymium site and decreases the average atomic radius of the rare earth site in $NdFe_{10}Si_2$. Consequently, the $ThMn_{12}$ phase is stabilized in (Nd, Zr)$Fe_{10}Si_2$.

This study can be summarized as follows.

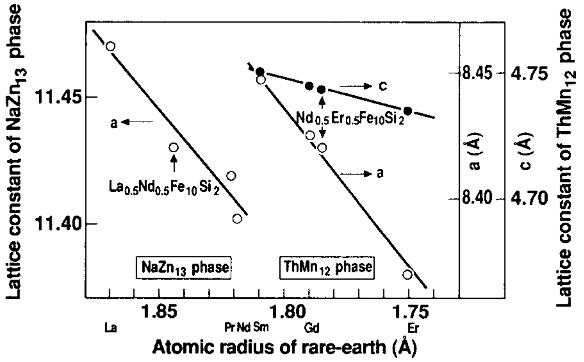
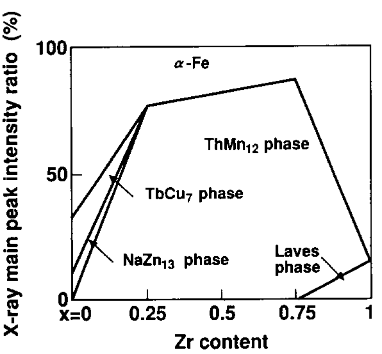


Fig. 2. Variation in lattice constants of $NaZn_{13}$ and $ThMn_{12}$ phases in $RFe_{10}Si_2$ with the atomic radius of rare earth element.



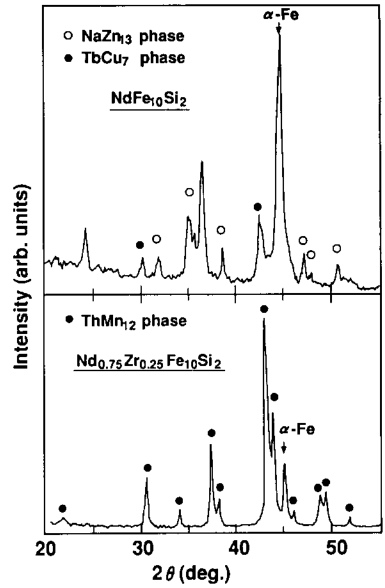


Fig. 3. Phases in rapidly quenched $Nd_{1-x}Zr_xFe_{10}Si_2$ ($V_r = 10$ m s^{-1}).

Fig. 4. X-ray diffraction patterns for rapidly quenched $NdFe_{10}Si_2$ and $Nd_{0.75}Zr_{0.25}Fe_{10}Si_2$ ($V_r = 10$ m s^{-1}).

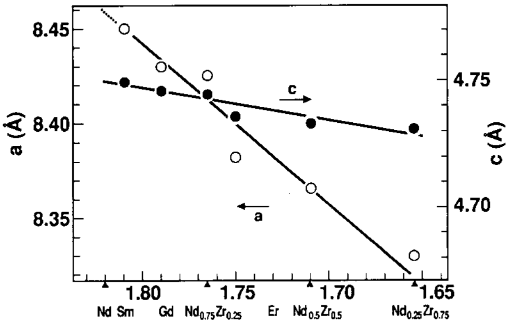


Fig. 5. Variation in the lattice constants of the $ThMn_{12}$ phase in $Nd_{1-x}Zr_xFe_{10}Si_2$ with the mean atomic radius of the rare earth site element.

The atomic radius of the element occupying the rare earth site is an important factor which controls the formation of $ThMn_{12}$ and $NaZn_{13}$ crystal structures in the $RFe_{10}Si_2$ system.

The $NaZn_{13}$ phase was found in $RFe_{10}Si_2$ (R ≡ La, Pr and Nd) in which the individual rare-earth atomic radii were larger than those of samarium.

On the contrary, the $ThMn_{12}$ phase was found in the system in which the individual rare earth atomic radii were smaller than those of neodymium in $RFe_{10}Si_2$. In the (Nd, Zr)$Fe_{10}Si_2$ system, zirconium occupies the neodymium site and facilitates the formation of the $ThMn_{12}$ phase owing to the decrease in the atomic radius of the neodymium site. Moreover, the amount of the

$ThMn_{12}$ phase increased with increasing zirconium content in $Nd_{1-x}Zr_xFe_{10}Si_2$ up to $x = 0.75$. These indicate that zirconium plays an important role in stabilizing the $ThMn_{12}$ structure.

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