

# Crystal structure and hydrogen absorption–desorption properties of $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$

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## Abstract

The novel compound  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  has been found in the Ca–Mg–Ni system, and its crystal structure has been investigated by X-ray diffraction and high-resolution transmission electron microscopy.  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  crystallizes in space group  $R\bar{3}m$  (No. 166); cell parameters:  $a = 4.9783(2)$  Å and  $c = 36.180(2)$  Å;  $Z = 3$ . The  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  structure has three blocks stacked along the  $c$  axis in one period, and each block is composed of two sub-blocks. One only contains one layer of  $[\text{CaMgNi}_4]$  units, and the other consists of one layer of  $[\text{CaMgNi}_4]$  units and one layer of  $[\text{CaNi}_5]$  units. Further investigations show that  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  has good kinetic properties but bad thermodynamic properties for hydrogen absorption–desorption. However, the Ca/Mg ratio of the  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$ -type compound can be adjusted within a wide range to improve the hydrogen absorption–desorption properties. As a result,  $\text{Ca}_{1.67}\text{Mg}_{3.33}\text{Ni}_{13}$  shows favorable thermodynamics and has good reversibility for hydrogen absorption–desorption.

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**Keywords:** Intermetallic compound; Crystal structure; X-ray diffraction (XRD); High-resolution electron microscopy (HREM); Hydrogen storage

## 1. Introduction

Intermetallic compounds in the La–Ni system, such as  $\text{LaNi}_5$ ,  $\text{La}_2\text{Ni}_7$  and  $\text{LaNi}_3$ , have been extensively investigated for hydrogen storage [1–3]. However, the hydrogen storage capacities of the binary compounds are not enough for practical applications. As the atomic weight of Ca is much lighter than that of La, some scientists have attempted to research the hydrogen storage properties of  $\text{CaNi}_5$  and  $\text{CaNi}_3$  [3,4].  $\text{CaNi}_5$  and  $\text{CaNi}_3$  are isostructural with  $\text{LaNi}_5$  and  $\text{LaNi}_3$ , respectively, because the atomic radius of Ca is close to that of La. It is interesting that  $\text{Ca}_2\text{Ni}_7$  crystallizes in space group  $R\bar{3}m$  (No. 166) [5], while  $\text{La}_2\text{Ni}_7$  crystallizes in space group  $P6_3/mmc$  (No. 194) [6]. The distinct structures are dependent on the slight difference between the atomic radii of Ca and La [7].

The La–Mg–Ni alloys, which were developed on the basis of the binary La–Ni compounds, have attracted more

attention over the past decade because of their high hydrogen storage capacities [8–12]. Similar to the binary compounds [13], the La–Mg–Ni compounds have superlattice structures, in which  $[\text{LaNi}_5]$  units (AB<sub>5</sub>-type) and  $[\text{LaMgNi}_4]$  units (Laves-type) stack along the  $c$ -axis in certain combinations [9,14]. The ordered Mg substitution leads to an improvement in the hydrogen storage properties. It is noteworthy that these layered structures can be analogously applied to the Ca–Mg–Ni system, such as the compound  $\text{CaMg}_2\text{Ni}_9$  [15]. Thus it is important to understand the correlation between hydrogen storage properties and structural characteristics in Ca–Mg–Ni compounds. Recently, the hydrogen storage properties of Ca–Mg–Ni alloys have also been studied by some scientists [16–19]. However, their investigations were mainly focused on (Ca,Mg)Ni<sub>2</sub> and (Ca,Mg)Ni<sub>3</sub> phases. The published literature is not enough to fully understand the nature of polytypic Ca–Mg–Ni compounds. It should be noted that the size of the Mg atom is smaller than that of Ca atom but larger than that of Ni atom. The occupation sites of Mg are particular in the Ca–Mg–Ni compounds, which usually

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lead to changes in crystal structures. As a result, new compounds may form that differ from the binary compounds. For example, the CsCl-type  $(\text{Ca}, \text{Mg})_2\text{NiH}_\delta$  hydride can be prepared by high-pressure synthesis [20]. Therefore, our present interest is to explore novel compounds in the Ca–Mg–Ni system and investigate the correlation between hydrogen storage properties and structural parameters.

Like those of La–Mg–Ni compounds, the layered structures of Ca–Mg–Ni compounds also consist of  $[\text{CaNi}_5]$  and  $[\text{CaMgNi}_4]$  units. Mg atoms preferentially form Laves-type  $[\text{CaMgNi}_4]$  units together with Ca and Ni [15]. According to Khan [21], the general formula for this series of compounds in the X–Mg–Ni systems (where X = Ca, Y and rare earth metals) can be expressed as  $[\text{XMgNi}_4]_n[\text{XNi}_5]$ , i.e.  $\text{X}_{n+1}\text{MgNi}_{5n+4}$ , where  $n$  is the number of  $\text{XNi}_5$  layers in the block. This means that each block in the structures consists of one layer of  $[\text{XMgNi}_4]$  unit and  $n$  layers of  $[\text{XNi}_5]$  units. Based on the above expression, Hayakawa deduced an extended expression  $m[\text{XMgNi}_4]_n[\text{XNi}_5]$ , i.e.  $\text{X}_{n+m}\text{Mg}_m\text{Ni}_{5n+4m}$ , for  $m$  layers of  $[\text{XMgNi}_4]$  units [14]. Up to now, however, only the compounds with  $m = 1$  were confirmed in the previous investigations [13–15,21]. In the present work, we have discovered a novel compound  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  with  $m = 2$  and  $n = 1$ , which is important for understanding the nature of crystal structures and the mechanism of hydrogen storage for this series of compounds.

In previous studies [13–15,21], the ternary compounds  $\text{X}_{n+m}\text{Mg}_m\text{Ni}_{5n+4m}$  preserve the initial structure of the corresponding binary compounds  $\text{X}_{n+2m}\text{Ni}_{5n+4m}$ . For example [14],  $\text{La}_2\text{MgNi}_9$  and  $\text{La}_4\text{MgNi}_{19}$  preserve the structures of  $\text{LaNi}_3$  and  $\text{La}_5\text{Ni}_{19}$ , respectively. In the present work, however, the corresponding binary compound  $\text{Ca}_5\text{Ni}_{13}$  for the new compound  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  is absent from the Ca–Ni system. Moreover, it is surprising that the  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  compound has the same space group  $R\bar{3}m$  as  $\text{Ca}_2\text{Ni}_7$  and the lattice parameters are close to those of  $\text{Ca}_2\text{Ni}_7$ . In spite of the similarities, the atomic coordinates of  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  and the atom ratios of  $(\text{Ca} + \text{Mg})/\text{Ni}$  are different from those of  $\text{Ca}_2\text{Ni}_7$ . Hence, the  $[\text{CaNi}_5]$  and  $[\text{CaMgNi}_4]$  units stack in a quite different manner.

In this paper, we report the structural characteristic and hydrogen absorption–desorption properties of  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$ . In the mean time, the crystal structure and hydrogen absorption–desorption properties of the  $\text{Ca}_3\text{MgNi}_{14}$  compound derived from  $\text{Ca}_2\text{Ni}_7$  are also presented for comparison. The possibility of improving the hydrogen storage properties by adjusting the Ca/Mg ratio is also reported.

## 2. Materials and methods

The  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$ ,  $\text{Ca}_3\text{MgNi}_{14}$ ,  $\text{Ca}_{1.67}\text{Mg}_{3.33}\text{Ni}_{13}$  and  $\text{CaMgNi}_7$  alloys were prepared by induction melting appropriate amounts of pure metals under an argon atmosphere. The losses of Ca and Mg during the induction melting were determined to be about 10 and 16 wt.%,

respectively, from repeated experiments. On the basis of stoichiometric amounts of starting materials, an extra 10 wt.% of Ca and 16 wt.% of Mg were therefore added to compensate for the losses of Ca and Mg during melting. The samples were remelted three times to ensure homogeneity. Then the samples were annealed at 550 °C for 2 days and subsequently 850 °C for 3 days under an argon atmosphere.

The alloys were crushed mechanically into powders of 300 mesh in a glovebox under a dry argon atmosphere. X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max 2500VL/PC diffractometer with  $\text{Cu } K_\alpha$  radiation at 50 kV and 150 mA. The XRD patterns were first indexed by TREOR90 [22]. The structure of  $\text{Ca}_3\text{MgNi}_{14}$  was derived from  $\text{Er}_2\text{Co}_7$  [23] in space group  $R\bar{3}m$ , while the structure of  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  was determined with the EXPO program [24,25] to be in space group  $R\bar{3}m$ . Based on the structural models, the XRD profiles were finally refined by the Rietveld program RIETAN-2000 [26].

The microstructures of the  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  and  $\text{Ca}_3\text{MgNi}_{14}$  compounds were observed by high-resolution transmission electron microscopy (HRTEM) using a JEM-2010 microscope. The samples used for HRTEM observations were prepared by dispersing powders in ethanol followed by ultrasonic vibration and then depositing the suspensions onto the copper grids coated with a layer of holey carbon film. Chemical compositions of the phases were measured by an energy dispersive X-ray spectrometry (EDS) within the JEM-2010 microscope.

To investigate the hydrogen absorption–desorption properties of the compounds, the powder samples were loaded into stainless steel containers and then placed in stainless steel autoclaves. The pressure–composition ( $P$ – $C$ ) isotherms were measured using a Sieverts-type apparatus. Before the measurements, the samples were activated by four hydrogen absorption–desorption cycles at 100 °C. During each cycle, the powder samples were hydrogenated under a hydrogen pressure of 3 MPa for 1 h and subsequently evacuated for 1 h.

## 3. Results and discussion

### 3.1. Crystal structures

For clear comparison between the structures of  $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$  and  $\text{Ca}_3\text{MgNi}_{14}$ , the Rietveld refinement of the observed XRD pattern for the  $\text{Ca}_3\text{MgNi}_{14}$  sample is first presented in Fig. 1. The sample contains a main phase  $\text{Ca}_3\text{MgNi}_{14}$  and the impurity phases  $(\text{Ca}, \text{Mg})\text{Ni}_3$ , Ni and CaO. For the Rietveld refinement, the structure model for the  $\text{Ca}_3\text{MgNi}_{14}$  was taken from the reported structure for  $\text{Er}_2\text{Co}_7$  [23] in space group  $R\bar{3}m$ . It can be seen that the diffraction pattern calculated is in good agreement with that measured. From the parameters refined by the Rietveld analysis, the phase abundance of  $\text{Ca}_3\text{MgNi}_{14}$ ,  $(\text{Ca}, \text{Mg})\text{Ni}_3$ , Ni and CaO were determined to be 81, 12, 5

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