

Single crystal X-ray diffraction study of  $\text{Ca}_2\text{NaCd}_2\text{V}_3\text{O}_{12}$  garnetAkira YOSHIASA<sup>1\*</sup>, Makoto Tokuda<sup>1</sup>, Hidetomo HONGU<sup>1</sup>, Tsutomu Mashimo<sup>1</sup>, Kazuake Iishi<sup>2</sup> and Akihiko Nakatsuka<sup>2</sup><sup>1</sup> Graduate School of Sciences and Technology, Kumamoto Univ. Kumamoto 860-8555, Japan<sup>2</sup> Graduate School of Sciences and Technology for Innovation, Yamaguchi Univ. 755-8611, Japan

## 1 Introduction

A garnet structure has been investigated for not only magnetic and optical properties but also the importance as component material of the Earth's mantle. The mean formal valences of vanadate garnets are represented by  $(\text{Ca}_2, \text{Na})_3^{+1.67}\text{M}_2^{+2}\text{V}_3^{+5}\text{O}_{12}$  ( $\text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ). The notable feature in vanadate garnets is that the V–O bond has a large covalency comparable to Si–O bond in silicate garnets. It is expected that the repulsion between cations across the shared edges of polyhedra in vanadate garnet is different from that in YAG and YIG. For understanding of the structural stability of garnets, in this study, we first report the structural data of  $\text{Ca}_2\text{NaCd}_2\text{V}_3\text{O}_{12}$  and discuss its structural features compared with previous study of vanadate garnet [1].

## 2 Experiment

The single crystal of  $\text{Ca}_2\text{NaCd}_2\text{V}_3\text{O}_{12}$  garnet was synthesized using a floating zone method. The characterization of synthesized crystal was examined using JEOL JCMA-733 electron microprobe analyzer. The crystal was ground into a sphere 0.12 mm in diameter for absorption correction. Single-crystal X-ray diffraction measurements were carried out with a four-circle diffractometer at the BL-10A beam line of the Photon Factory, Tsukuba, Japan, using monochromatized synchrotron X-ray ( $\lambda = 0.70006 \text{ \AA}$ ) radiation. The unit-cell parameters at each temperature were determined by the least-squares method from a set of 25 reflections. During the least-square refinements a correction for isotropic extinction was applied. After several cycles of refinements the displacement parameters were converted from isotropic to an anisotropic model. Final  $R$  and  $wR_2$  values were 0.0159 and 0.0199, respectively [2].

## 3 Results and Discussion

The effect of ionic radius of Y-site cation causes the increase of cation–cation distances and finally the increase of the lattice constant  $a$ . As one of features of vanadate garnet, cation–cation distances are long as compared with the one of silicate garnets. For vanadate garnets, the ionic radius of cation in X-, Y-, and Z-site are relatively larger and cations in X- and Y-site has less valence electrons as compared with that of other general garnets[1]. Therefore, it is thought that the repulsions of (Ca, Na)–(Ca, Na) and (Ca, Na)–Cd are fairly weaker than the repulsions of X–X and X–Y of other garnets.

We consider the comparison of the vanadate garnet ( $\text{Y} = \text{Cd}$ ) with other vanadate garnets ( $\text{Y} = \text{Mg}, \text{Zn}, \text{and Mn}$ ). The first structural feature is that the dodecahedral–

dodecahedral shared edge length O4–O6 in  $\text{Y} = \text{Mg}, \text{Zn}$ , and  $\text{Mn}$  is considerably longer than the unshared dodecahedral edge length O4–O7. This feature comes from the weak repulsion between cations in X-site and Y-site. And also, the geometric constrains derived from the size of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in X-site and M cations in Y-site makes O4–O6 distance elongate anomalously. This geometric constrain can be seen with in ugrandite garnets. On the other hands, the shared dodecahedral edge O4–O6 distance in  $\text{Y} = \text{Cd}$  become shorter than the unshared edge O4–O7 distance, as shown in Fig. 1 This result is similar to the tendency for pyralspite garnet. The O4–O7 distance maintain constant values against size of M cations in Y-site [1].

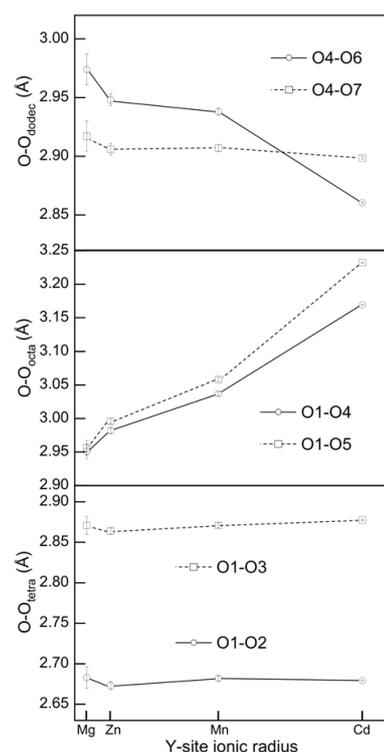


Fig. 1: The shared (open circles) and unshared (open squares) oxygen–oxygen edge lengths plotted against the ionic radii in the Y-site cation (Mg, Zn, Mn and Cd).

## References

[1] M. Tokuda, A. Yoshiasa, T. Mashimo, K. Iishi and A. Nakatsuka, Acta Crystallographica Section C74 (2018), 460–464 <https://doi.org/10.1107/S2053229618003741>

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