

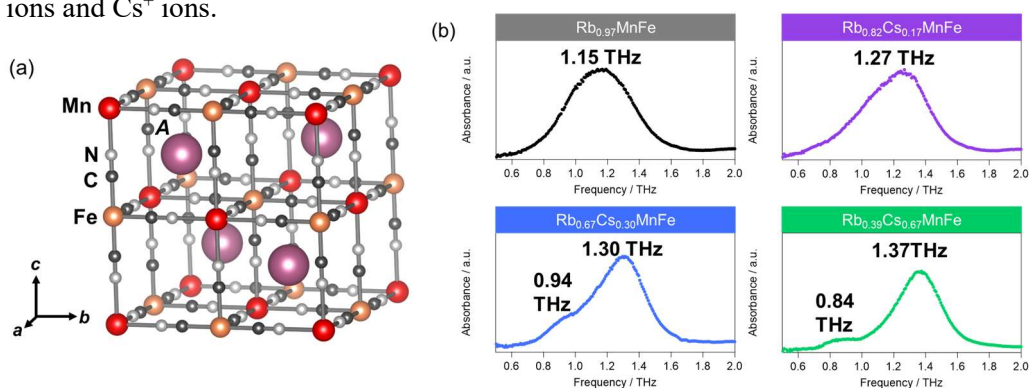
## The effect of the co-substitution with heavy alkali cations for THz wave absorption properties with charge-transfer induced phase transition of cyanido-bridged metal assemblies

(Graduate School of Science, University of Tokyo) ○Yuuki Mineo, Koji Nakabayashi, Kenta Imoto, Kosuke Nakagawa, Marie Yoshikiyo, Shin-ichi Ohkoshi

**Keywords:** Terahertz spectroscopy; cyanido-bridged metal assembly

A rubidium manganese hexacyanoferrate, one of cyanido-bridged metal assemblies, exhibits a variety of the physical properties, such as a charge-transfer phase transition, photo-induced magnetization, and so on.<sup>1,2</sup> Substitution of heavy alkali cations can be one way to affect such various physical properties. Additionally, our laboratory recently reported that cesium manganese hexacyanoferrate, an isostructural analogue of rubidium manganese hexacyanoferrate, shows THz wave absorption at 1.4 THz due to the phonon modes of  $\text{Cs}^+$  ions encapsulated in the three-dimensional cyanido-bridged lattice.<sup>3</sup> Therefore, we investigated the effect of the substitution of heavy alkali cations on the THz wave absorption properties in the series of the three-dimensional cyanido-bridged Mn–Fe assemblies.

The powder X-ray diffraction pattern and the Rietveld analysis revealed that the co-substituted sample,  $\text{Rb}_{0.82}\text{Cs}_{0.17}\text{Mn}[\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$  ( **$\text{Rb}_{0.82}\text{Cs}_{0.17}\text{MnFe}$** ), has a cubic structure in a space group of  $F\bar{4}3m$  (Fig. 1a). In magnetic measurements,  **$\text{Rb}_{0.82}\text{Cs}_{0.17}\text{MnFe}$**  shows a charge-transfer phase transition between the high temperature (HT) phase and the low temperature (LT) phase. THz wave absorption properties were revealed by using Terahertz time-domain spectroscopy (THz-TDS). While the isostructural compound of Rb,  $\text{Rb}_{0.97}\text{Mn}[\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$  ( **$\text{RbMnFe}$** ), shows the THz wave absorption at 1.15 THz,  **$\text{Rb}_{0.82}\text{Cs}_{0.17}\text{MnFe}$**  is at 1.27 THz (Fig. 1b). The difference of the absorption frequency is due to the larger ionic radii of the  $\text{Cs}^+$  ions than that of the  $\text{Rb}^+$  ions despite the comparable lattice constants for  **$\text{RbMnFe}$**  and  **$\text{Rb}_{0.82}\text{Cs}_{0.17}\text{MnFe}$** . Moreover, the content ratio of  $\text{Cs}^+$  ions increase, the absorption spectrum shows the shift of the absorption frequency to higher as well as the appearance of the shoulder of another peak. The absorption spectra of the co-substituent compounds did not consistent with the sum of the absorption spectra of isolated compounds of  $\text{Rb}^+$  ions and  $\text{Cs}^+$  ions.



**Fig. 1.** (a) The crystal structure of  $\text{AMnFe}$  ( $A = \text{Cs}^+$  or  $\text{Rb}^+$ ). (b) THz wave absorption spectra of  **$\text{RbMnFe}$**  and the  $\text{Cs}^+$ -substituted compounds at room temperature.

- 1) S. Ohkoshi, T. Matsuda, H. Tokoro, and K. Hashimoto, *Chem. Mater.* **2005**, 17, 1, 81–84.
- 2) H. Tokoro, T. Matsuda, T. Nuida, Y. Moritomo, K. Ohoyama, E. Loutete-Dangui, K. Boukheddaden, and S. Ohkoshi, *Chem. Mater.* **2008**, 20, 423–428.
- 3) S. Ohkoshi, M. Yoshikiyo, A. Namai, K. Nakagawa, K. Chiba, R. Fujiwara, H. Tokoro, *Sci. Rep.*, **2017**, 7, 8088.