

THz wave absorption modulated by charge-transfer induced phase transition of cyanido-bridged metal assemblies

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Cyanido-bridged metal assemblies are attractive compounds due to various physical properties, such as ferromagnetism, charge-transfer phase transition, photo-induced magnetization, and second harmonic generation.^{1,2} Recently, we reported that $\text{Cs}_x\text{Mn}[\text{Fe}(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$ exhibits low-frequency THz wave absorption at 1.4 THz due to phonon-mode oscillations of Cs^+ ions in the voids of the isotropic three-dimensional lattice.³ Based on the concept, modification of the crystal structure or substitution of the heavy alkali cation are considered to be effective in controlling THz wave absorptions. Therefore we studied the THz wave absorption properties of $\text{Rb}_{0.97}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.99} \cdot 0.5\text{H}_2\text{O}$ (**RbMnFe**), which shows a charge-transfer phase transition.

The Rietveld analysis of the PXRD pattern of **RbMnFe** revealed that it has a cubic structure with a space group of $F\bar{4}3m$ in the high temperature (HT) phase. As temperature decreases, the distances between Fe and Mn in *ab* plane shrink and the crystal structure changes into a tetragonal structure with a space group of $I\bar{4}m2$ in the low temperature (LT) phase. Terahertz time-domain spectroscopy reveals that **RbMnFe** has a THz wave absorption at 1.15 THz at room temperature, while the frequency is 1.41 THz in the LT phase. This change should be due to the shrinkage of the lattice including Rb^+ ions with the decrease of the temperature. By limiting the range of motion of Rb^+ ions, the oscillation becomes faster, resulting in a higher frequency. Moreover, THz wave absorption measurements were also performed for the compounds which contain both Rb^+ ions and Cs^+ ions, $\text{Rb}_{0.82}\text{Cs}_{0.17}\text{Mn}[\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$ (**Rb_{0.82}Cs_{0.17}MnFe**), $\text{Rb}_{0.67}\text{Cs}_{0.30}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.99} \cdot 0.6\text{H}_2\text{O}$ (**Rb_{0.67}Cs_{0.30}MnFe**), and $\text{Rb}_{0.38}\text{Cs}_{0.59}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.99} \cdot 0.7\text{H}_2\text{O}$ (**Rb_{0.38}Cs_{0.59}MnFe**). As a result, the absorption frequency becomes higher as the increase of the quantity of Cs^+ ions because of larger ionic radius of Cs^+ ions in the limited space than that of Rb^+ ions.

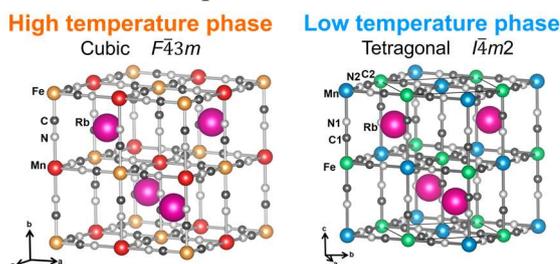


Fig. 1. The crystal structure of **RbMnFe**.

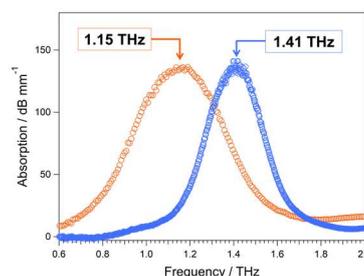


Fig. 2. THz wave absorption spectra of **RbMnFe** in the HT phase (orange) and in the LT phase (blue).

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