

Cd Doping in the Giant Dielectric Constant Material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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Introduction: The cubic perovskite-related material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has an extremely high static dielectric constant at room temperature, $\epsilon_0 \sim 10^4$, when measured at radio frequencies [1]. However, below ~ 100 K the dielectric constant drops by about two orders of magnitude to $\epsilon_0 \sim 100$, but no lattice distortion is observed [2]. When Cd is substituted for Ca, the dielectric constant is much lower, $\epsilon_0 \sim 500$. Optical measurements on $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ showed that there were a number of phonon anomalies at low temperature [3]. The doping series $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ has been investigated to try and determine the role that Cd plays in the lowering the value for the dielectric constant.

Methods and Materials: The reflectance of polished dense ceramics of $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ were measured at a near-normal angle of incidence over a wide frequency range (~ 30 to 5000 cm^{-1}) at room temperature on a Bruker IFS66v/S FTIR spectrometer using an *in-situ* overcoating technique [4].

Results: The conductivity is determined from a Kramers-Kronig analysis of the reflectance and is shown in Fig. 1. For $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ there are 10 vibrational modes observed (11 are expected from group theory). However, with Cd incorporation there are large changes that occur in the low-frequency vibrational structure, indicating that these modes involve displacements of the Cd atoms. While the high-frequency modes (above 300 cm^{-1}) show relatively change, a new mode is observed at $\sim 470\text{ cm}^{-1}$ which becomes more prominent at heavier Cd dopings. (The Cd atom has a much larger electronegativity than Ca; otherwise the two ions are quite similar.) The mode at 470 cm^{-1} is something of a mystery as both density functional theory and normal coordinate analysis calculate a mode of significant optical strength to lie at precisely this point; the other calculated frequencies agree very well with the experimental values. The high value for the dielectric constant is thought to arise from the high-degree of twinning in this material, which leads to a boundary-layer capacitance effect and a large effective dielectric constant [1,3]. It is thought that the incorporation of Cd for Ca reduces, but does not remove, the twinning in this system, thereby leading to a reduction in the low-frequency values for the dielectric constant. The evolution of the mode at $\sim 470\text{ cm}^{-1}$ appears to act as a measure of this process.

Conclusions: The optical properties of the giant dielectric materials $\text{Ca}_{1-x}\text{Cd}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ have been studied for $x=0, 0.3, 0.5, 0.7$ and 1 . The dielectric constant at radio frequencies is observed to drop with Cd substitution, while at the same time a new vibrational mode is observed at $\sim 470\text{ cm}^{-1}$. It is thought that the appearance of this new mode is a reflection of the reduced degree of twinning in the system.

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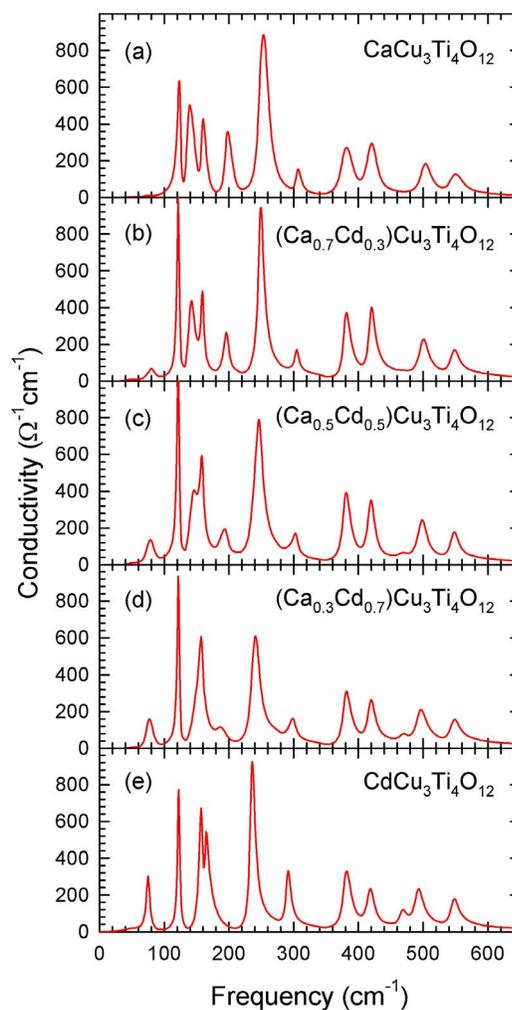


Figure 1: The optical conductivity at room temperature for various levels of Cd doping.