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Heat Induced Charge Transfer in the Solid Solution $Co_{3-x}T_x[Fe(CN)_6]_2\,yH_2O$ with T = Mn, Ni, Cu, Zn and Cd

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Cobalt hexacyanoferrates have a relatively low energy barrier for the charge transfer between cobalt and iron atoms. That energy barrier can be overcome by irradiation with light in the ultraviolet-blue region or through the sample heating. Such feature for that charge transfer process is determined by structural and compositional factors. In this contribution the role of a second metal partially substituting to Co in the material composition on the heat induced charge transfer is studied. Samples of the solid solution $Co_{3-x}T_x[Fe(CN)_6]_2yH_2O$ with T = Mn, Ni, Cu, Zn and Cd, were prepared by a simple synthetic route and their behavior on moderate heating, from 80 to 160 °C, was evaluated. The behavior of the solid solution on heating was followed by infrared, X-ray diffraction and Mössbauer data. The heat induced charge transfer appears to be favored once the crystal water is removed, when the metal-metal interaction, through the CN bridges, reaches its maximum strength. From this fact, when a metal like Cu, Zn and Cd, with a relatively weak interaction with the coordinated water molecules and, as a consequence, with a low dehydration temperature, is present in the material structure, a lower activation energy is required to be able the heat induced charge transfer. Even in the presence of a second divalent transition metal occupying a fraction of the structural sites for Co, the charge transfer was observed, which is particularly pronounced in the 120–140 °C temperature range. The heat-induced charge transfer was also evaluated from the photo-induced inverse process in the heated samples using photo-acoustic spectroscopy.

1. Introduction

The mixed valence states are common in solid compounds containing transitions metal ions. Their electronic structure and related optical, thermal, electrical and

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