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Synthesis, Structural Characterization and Thermal Stability of Nanocrystalline Rare-Earth Chromates ($RECrO_4$) and Rare-Earth Chromites ($RECrO_3$)

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In this study, a series of nanocrystalline single-phasic $RECrO_4$(La–Lu, except Ce and Pm) compounds have been synthesized by glycine-nitrate combustion method in fuel-deficient ratio. The compounds were characterized by techniques such as XRD (X-ray diffraction) and TEM (Transmission Electron Microscopy). $RECrO_3$ series of compounds were obtained after decomposition of the respective $RECrO_4$ compounds. XRD studies of the respective products, confirms the formation of mono-phasic rare-earth chromates ($RECrO_4$) and chromites ($RECrO_3$). Thermal behavior of all the rare-earth chromates ($RECrO_4$) was studied using simultaneous TG–DTA. Decreasing trend was observed in decomposition temperature from $LaCrO_4$ to $LuCrO_4$. Stability of $RECrO_4$ compounds have been correlated with structural, thermodynamics and heat transport aspects of the respective compounds.

Keywords: Nanocrystalline, Rare-Earth Chromate, Rare-Earth Chromite, Glycine-Nitrate Combustion Synthesis.

1. INTRODUCTION

Rare-earth chromates ($RECrO_4$) are the special class of oxides with attractive crystallographic and magnetic properties.[1] Only few studies have been carried out concerning the $RECrO_4$ compounds, probably due to the difficulty in preparing the phase pure sample free from corresponding $RECrO_3$. These compounds contain the unusually high valence state Cr(V) ion which decomposes at high temperature to yield corresponding rare-earth chromites ($RECrO_3$) with perovskite type lattice. Few $RECrO_4$ samples have been prepared using correlated nitrates or acetates as original materials.[2–5] In all these synthesis methods an oxygen flow was used in order to stabilize the 5+ oxidation state in the chromium. There are also few reports on the preparation of $RECrO_4$ by decomposition of organic complex of corresponding rare-earth.[1, 5–9] Synthesis of such organic rare-earth precursor is not only difficult but synthesis procedure becomes more complicated when the product is required in the nano regime. There are very few reports on single phasic synthesis of nanocrystalline $RECrO_4$.[10, 11] On the other hand, rare-earth chromites ($RECrO_3$) are being contemplated to be new multiferroics possessing both ferromagnetic and ferroelectric properties and thus becoming increasingly important in view of their potential applications and have received wide attention in recent years.[12–15] There are very few other metal oxides, which are known to exhibit multiferroic nature such as $YMnO_3$[16], $BiFeO_3$,[17] $BaTiO_3$[18], PZT[19] etc.

In order to synthesize nanocrystalline $RECrO_4$ having Cr in 5+ oxidation state, needs a very mild chemical reaction to be developed which can stabilize the desired oxidation state of chromium. $RECrO_3$ synthesized by conventional solid-state method often gives product with impurity of reactants. Hence, it is a difficult to synthesize phase pure nanocrystalline $RECrO_4$ and $RECrO_3$. In view of this, we report the synthesis of single-phasic nanocrystalline $RECrO_4$ (RE = La to Lu except Ce, and Pm) by gel-combustion method.[20, 21] $RECrO_3$ compounds have been synthesized by a controlled decomposition of corresponding $RECrO_4$ as the precursor.

2. EXPERIMENTAL DETAILS

The AR grade reactants used are rare-earth oxide (RE_2O_3; RE = La–Lu) and chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$). The rare-earth oxide was dissolved in 50% HNO_3 to

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