

Synthesis, structure and crystallization of dysprosium carbonate phases

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Dysprosium plays an important role in a wide variety of crucial electronic devices as well as in emerging clean energy technologies [1]. It has been identified as the most in-demand rare-earth element (REE) by the US Department of Energy and its scarcity may affect clean energy technology development in the short (present-2015) and medium (2015-2025) term [2]. More than 90% of the global supply of dysprosium comes from the REE deposit in Bayan Obo (China), which contain a variety of ore minerals, many of them REE-bearing carbonates [3]. Due to their economical importance, the understanding of the origin and distribution of REE-bearing minerals, and REE-carbonates in particular, has become a research priority that necessitates a quantitative understanding of their formation and crystallization pathways. In the case of Dy, only dysprosium carbonate hydroxide/oxide ($DyCO_3(OH)$ and $Dy_2O_2CO_3$ [4]) have been structurally determined. Nevertheless, their crystallization pathways have so far not been quantified and in this study we have, for the first time, investigated the crystallization pathways of Dy-carbonates both in air and in solution and we have done this over a range of temperatures (21- 750 °C).

We performed experiments in stirred reactors at 21 °C by mixing equimolar solutions of $DyCl_3 \cdot H_2O$ (Alfa Aesar, 99% purity) and Na_2CO_3 . Immediately upon mixing of the starting solutions a white gel formed and aliquots of this gel-like material were treated using three different approaches: i) one batch was dry-heated in air using thermodiffraction at temperatures between 25 and 750 °C. The other two batches were aged in their native solution either at ii) 21 °C for up to two months, or iii) hydrothermally at 90, 165 or 220 °C for up to 15 days. The hydrothermal treatments were carried out in stainless steel Teflon-lined reactors under saturated water vapour pressures. The initial gel, various intermediates and the end product solids were characterized with X-ray diffraction, Fourier transform infrared spectroscopy, scanning and transmission electron microscopy, thermogravimetric analysis and magnetic techniques.

Our results show that the precipitation of dysprosium carbonate from solution at room temperature proceeds via the formation of a highly hydrated, nanoparticulate and amorphous dysprosium carbonate phase, with a composition of $Dy_2(CO_3)_3 \cdot 4H_2O$. This amorphous dysprosium carbonate remains exceptionally stable under dry atmospheric conditions and only crystallizes to Dy_2O_3 above 550 °C. However, it transforms to various crystalline dysprosium carbonates when reacted in solution. The crystalline product depends on the reaction temperature and reaction times. At ambient temperature the amorphous precursor transforms into an poorly crystalline and metastable tengerite-type phase, $Dy_2(CO_3)_3 \cdot 2-3H_2O$. When heated hydrothermally above 90 °C the same phase forms, but with the solid product exhibits a much increased crystallite size. The tengerite-type phase, $Dy_2(CO_3)_3 \cdot 2-3H_2O$ transforms at 165 °C to a kozelite-type phase, $DyCO_3(OH)$ only after 15 days while at 220 °C the same reaction only takes 12 hours and the crystalline size of the end product is drastically increased. Both the amorphous phase and the high temperature crystalline $DyCO_3(OH)$ reveal a paramagnetic behaviour in the temperatures range between 1.8 to 300 K.

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