

Magnetism and Large Magnetocaloric Effect of Zircon and Scheelite Polymorphs of RCrO_4 (R=Rare Earth) Oxides

R. Sáez Puche¹, A. Dos santos-García², E. Palacios³, M. Castro³ and R. Burriel³

¹*Dep. de Química Inorgánica, Universidad Complutense de Madrid, 28040 Madrid Spain*

²*Dep. Ingen. Mecánica, Química Diseño Industrial, ETSIDI, U.P.M, 28012 Madrid, Spain*

³*Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain*

Corresponding autor e-mail: rsp92@ucm.es

RCrO_4 oxides (R = rare earth), which can be prepared at moderate temperatures under atmospheric pressure in oxygen flow, crystallize with the zircon-type structure showing tetragonal symmetry, S.G. $I4_1/amd$. When the zircon RCrO_4 polymorphs were heated at 450 °C at 45 kbar, they transform into the corresponding RCrO_4 scheelite phase, S.G. $I4_1/a$ (1, 2). The coexistence of two paramagnetic ions $\text{Cr}^{5+}(3d^1)$ and $\text{R}^{3+}(4f^n)$ constitutes the ideal scenario to study the 3d-4f magnetic interactions and this could justify the relatively high ordering temperatures that present these oxides in comparison with the analogous RVO_4 and RPO_4 compounds where R is the only paramagnetic ion (2, 3). The study of the magnetic properties of these oxides reveals that the zircon phases behave as ferromagnetic (FM), while the scheelite derivatives show an antiferromagnetic (AFM) behavior. These changes in the sign of the magnetic interactions in going from zircon to scheelite has been explained by considering the change in the R-O-Cr bond angles which is the main pathway for the exchange interactions taking place in these compounds. A detailed analysis of the structure have been done to explain these dramatic changes in the magnetic behavior and to establish valuable relationships structure-magnetic properties. The magnetic structures of both families of compounds have been established from neutron diffraction data.

Magnetic cooling processes based on adiabatic demagnetization of paramagnetic salts or FM compounds, known as magnetocaloric effect (MCE), represents a new refrigeration technology. It is environmental friendly and more efficient compared to the classical one based on vapor compression cycles. In this sense, a large MCE has been very recently reported in the GdCrO_4 zircon polymorph, where the isothermal entropy change reaches a maximum of 29 J/kg·K at 22 K for a magnetic field variation of 0 - 9 T (4).

In this work the MCE of zircon and scheelite RCrO_4 polymorphs is presented, with special emphasis on oxides where R presents large magnetic moments, namely from Gd to Tm. The MCE effect has been determined from M vs. H curves at different temperatures and from C_p vs. T at different magnetic fields. As expected, due to the FM ordering of the zircon polymorphs, they show a larger MCE than the homologous AFM scheelite phases.

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