Journal of Solid State Chemistry 228 (2015) 183–188

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Structural chemistry and magnetic properties of $Y_2CoGe_4O_{12}$

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ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form
21 April 2015
Accepted 22 April 2015
Available online 30 April 2015

Keywords:
Mixed-metal germanate
Neutron diffraction
EXAFS
Structure determination

ABSTRACT

Polycrystalline $Y_2CoGe_4O_{12}$ has been prepared by standard ceramic methods. The crystal structure (space group $P4/nbm$; $a=9.8465(2)$, $c=4.92986(9)$ Å) consists of metal-rich layers separated from each other by Ge_4O_{12} groups comprised of four corner-sharing GeO_4 tetrahedra. Two cation sites lie within the layers; an eight-coordinate site occupied by yttrium and a six-coordinate site occupied by a 1:1 disordered distribution of yttrium and cobalt. Neutron diffraction revealed two-fold disorder on the oxide sublattice; this has been elucidated using Co *K*-edge EXAFS spectroscopy. The availability of two sites allows each oxide ion to accommodate the coordination preferences of its single Co/Y neighbour; the GeO_4 tetrahedra distort to absorb any consequent strain. The octahedron of anions around each Co^{2+} cation shows a pseudo-tetragonal distortion with a strain $(Co–O)_{eq}–(Co–O)_{ax}/(Co–O)_{eq} = -0.173$. This results in an unusually large effective magnetic moment of 6.05 μ_B per Co^{2+} cation.

1. Introduction

Yamane et al. [1] and Zubkov et al. [2] have previously described the crystal structure of compositions in the family $Ln_2M^{2+}Ge_4O_{12}$, where *Ln* is a lanthanide (a term that we shall take to include yttrium), and *M* is Ca, Mn or Zn. The structure can be considered to consist of metal-rich layers separated from each other by Ge_4O_{12} groups made up of four corner-sharing GeO_4 tetrahedra. Two crystallographically distinct cation sites lie within the layers; an eight-coordinate site occupied exclusively by *Ln* and a six-coordinate site occupied by a disordered arrangement of *Ln* and *M*, see Fig. 1. The structure adopts the tetragonal space group $P4/nbm$. Zubkov et al. were motivated by an interest in the optical properties of $Ln_2M^{2+}Ge_4O_{12}$ [3–5]. They synthesised a number of different compositions and characterised them using X-ray powder diffraction. The temperature dependence of the magnetic susceptibility of $Eu_2MnGe_4O_{12}$ was measured in an attempt to identify the oxidation states of the two metals, but no other magnetic data have been reported.

The occupation of a six-coordinate site by a disordered arrangement of Ca^{2+} and Ln^{3+} has been seen previously, for example in Ca_2HoRuO_6 [6], but the ionic radii of lanthanide cations and divalent cations of the first-row transition metals, for example Mn^{2+}, are usually sufficiently different to exclude such mixing. We have therefore begun to explore which combinations of *Ln* and *M* can be accommodated in this crystal structure. In contrast to Zubkov et al., our study was motivated by an interest in the magnetic properties of these compositions. In this paper we describe a detailed structural study of $Y_2CoGe_4O_{12}$ that was undertaken following the observation of apparently anomalous magnetic behaviour. EXAFS was used to determine the local environments around the cobalt cations in order to facilitate a comparison with the average environment around the six-coordinate site as determined by neutron diffraction.

2. Experimental

Attempts were made to prepare polycrystalline samples of $Ln_2M^{2+}Ge_4O_{12}$ ($M=$Fe, Co) by heating stoichiometric mixtures of GeO_2, dried Ln_2O_3 and either Fe_3O_4 or Co_3O_4 in air for ~100 h, initially at 1050 °C. All compositions apart from $Y_2CoGe_4O_{12}$ were subsequently heated at 1075 °C. In the light of the results of the magnetic study of $Y_2CoGe_4O_{12}$ it was decided to study the magnetic behaviour of the magnetically-diluted compositions $Y_2Co_{1-y}Ca_yGe_4O_{12}$ $(0<y<1)$. $CaCO_3$ was used as a starting material in the syntheses of these compounds, which took 150 h to complete at a temperature of 1075 °C; the reactants were reground every 20 h. The progress of all the reactions, the purities of the products and, in the case of a successful reaction, the crystal structure of the product were studied using X-ray powder diffraction. Data collected at room temperature on a Panalytical X'Pert

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http://dx.doi.org/10.1016/j.jssc.2015.04.033
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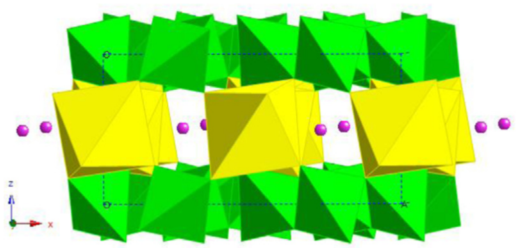

Fig. 1. The crystal structure of $Ln_2MGe_4O_{12}$; green tetrahedra represent GeO_4 groups, yellow octahedra represent Ln/MO_6 groups and lilac circles represent *Ln* atoms on the 2*b* site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

diffractometer operating with Cu $K\alpha_1$ radiation were analysed by the Rietveld method [7], as implemented in the FullProf program suite [8]. The magnetic susceptibility of selected compositions was measured over the temperature range $2 < T/K < 300$ using a Quantum Design MPMS 5000 SQUID magnetometer. Data were collected on warming in a field of 100 Oe after cooling the sample both in the absence of an applied field (zero-field cooled, ZFC) and in the measuring field (field cooled, FC).

On the basis of the results of these measurements one sample, $Y_2CoGe_4O_{12}$, was selected for further study. The diffractometer D2b at ILL Grenoble was used to collect neutron powder diffraction data at a wavelength of ~1.59 Å. The sample was contained in a vanadium can. Data were collected over the angular range $10 < 2\theta$ (deg) < 155 with a step size $\Delta 2\theta = 0.05°$. They were analysed by the Rietveld method as implemented in the GSAS program package [9]. X-ray absorption spectra were collected on beamline B18 at the Diamond Light Source from the same *Ln*=Y sample. A well-ground sample was diluted with cellulose before being pressed into a pellet of 8 mm diameter under a pressure of 1.5 tonnes. Data were collected at the Co *K*-absorption edge in transmission using the QEXAFS mode (that is, data were collected as the monochromator scanned in energy continuously, without stopping other than at the limits of the required energy range). The beamline was set-up to use the Si(111) crystals in the monochromator and the Cr coating of the different mirrors. Data were collected between room temperature and 100 K using a liquid nitrogen cryostat. Here we will present only the results obtained at 300 K and 100 K as no structural transitions were observed in the intermediate temperature region. Data analysis was carried out using the programs Athena and Artemis [10].

3. Results

Syntheses involving iron were unsuccessful and will not be discussed further. Bragg peaks attributable to the phase described by Zubkov et al. [2] could be seen in the X-ray diffraction patterns of $Ln_2CoGe_4O_{12}$ for *Ln*=Y, Gd, Tb, Ho, Er, Yb and Lu. However, for all lanthanides other than yttrium the samples contained a significant (2.9–6.4%) level of $Ln_2Ge_2O_7$ impurity. In the case of $Y_2CoGe_4O_{12}$, X-ray diffraction showed the reaction product to consist largely of a phase isostructural with those prepared by Zubkov et al., with only ~1 wt% $Y_2Ge_2O_7$ present. No impurity was detected when the ratio of the reactants was modified to give a nominal composition of $Y_{1.95}CoGe_4O_{12}$ and this sample was used in our subsequent studies. The unit cell parameters refined to $a = 9.8465(2)$, $c = 4.92986(9)$ Å. The temperature dependence of the molar magnetic susceptibility of this sample is shown in Fig. 2. No phase transition is apparent in the measured temperature range. Fitting the data in the range $150 < T/K < 300$ to the Curie–Weiss law resulted in a Weiss temperature $\theta = -27.4(4)$ K and a Curie constant $C = 4.581(9)$ cm^3 K mol^{-1}. The latter leads to a value of 6.05 μ_B for the effective magnetic moment of the cobalt cations. This result was reproduced in measurements made on independently-synthesised samples.

The neutron diffraction pattern of the yttrium-containing sample could be accounted for in the space group *P*4/*nbm*; no reflections attributable to an impurity phase were detected in a visual inspection of the data. In the analysis of these data the unit cell parameters were held constant at the values determined from the X-ray data and the wavelength of the neutron beam was refined. Initially single-phase refinements were carried out using the structural model described by Zubkov et al., with a disordered distribution of yttrium and cobalt on the 4*f* site. The yttrium content of the 2*b* and 4*f* sites was refined but no significant deficiency was detected on either site. During the course of the data analysis it was noted that the displacement parameter of the oxide ion on the 16*i* site in Zubkov's model was relatively large. This atom was therefore disordered over two half-occupied 16*i* sites, O2 and O3, which were constrained to have the same displacement parameter. Despite the absence of clearly visible reflections from a second phase, in order to allow for the yttrium-deficient composition of the reaction mixture, the phase $CoGeO_3$ [11] was included in our final refinements. The presence of this weakly-scattering phase was anticipated because it has been formed in relatively large amounts during our attempts to synthesize related compounds under similar conditions. Our refinements showed that in this case it constituted 0.6(1) wt%, that is 2.5 mol%, of the reaction product. The final observed and calculated diffraction patterns are shown in Fig. 3; the agreement factors are $R_{wpr} = 5.0\%$, $\chi^2 = 4.9$. The resulting structural parameters are listed

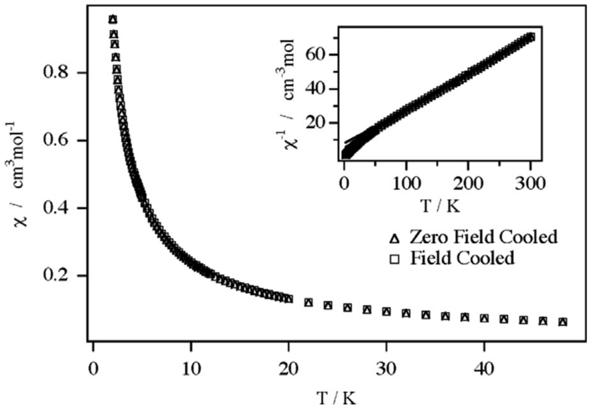

Fig. 2. Temperature dependence of the molar magnetic susceptibility of $Y_2CoGe_4O_{12}$. The inverse molar susceptibility is shown in the inset.

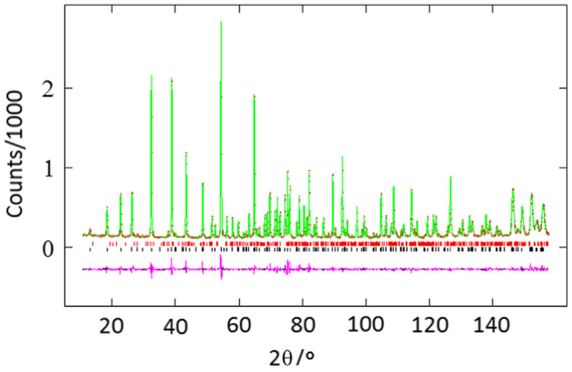

Fig. 3. Observed and calculated neutron diffraction patterns; a difference curve is also shown. The upper and lower sets of reflection markers correspond to $CoGeO_3$ and $Y_2CoGe_4O_{12}$, respectively.