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Crystal growth, structure and magnetic properties of the double perovskites Ln_2MgIrO_6 (Ln=Pr, Nd, Sm–Gd)

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ABSTRACT

Single crystals of double-perovskite type lanthanide magnesium iridium oxides, Ln_2MgIrO_6 (Ln=Pr, Nd, Sm–Gd) have been grown in a molten potassium hydroxide flux. The compounds crystallize in a distorted 1:1 rock salt lattice, space group $P2_1/n$, consisting of corner shared MO_6 (M=Mg^{2+} and Ir^{4+}) octahedra, where the rare earth cations occupy the eight-fold coordination sites formed by the corner shared octahedra. Pr_2MgIrO_6, Nd_2MgIrO_6, Sm_2MgIrO_6, and Eu_2MgIrO_6 order antiferromagnetically around 10–15 K.

1. Introduction

Perovskites are one of the most widely studied families of oxides owing greatly to their synthetic variability, compositional flexibility and intriguing properties. The discovery of new perovskites can be carefully postulated based on radius ratio rules. There is a vast library of known compositions with the general formula ABO_3, where A is large electropositive atom and B is a smaller atom [1], which is undoubtedly directly related to the ease with which cationic substitutions can be achieved in this family. The number of possible compositions can be further expanded when one allows for consideration of the compounds that adopt the double perovskite structure, with general formula $A_2BB'O_6$. Similarly, if one allows for cation substitutions with two different metals on the A-site such as in compounds with the formula $AA'BB'O_6$ as exemplified by $BaLaCoIrO_6$ [2], B-site substitutions of two metals of similar size and charge as in Nd_2BOsO_6, (B=Na, Li) [3,4], or B' site substitutions of two metals of similar size and available charge as demonstrated by $La_2NaB'O_6$ (M=Ru, Ir) [5–7], it becomes very apparent that not only are there already a large number of compositions in existence, but also that many new compositions can be prepared. In fact, taking into consideration radius ratio rules, the solid state chemist can confidently postulate the existence of an abundance of potential compositions in the ABO_3 [8] family and a seemingly unquantifiable number of compositions in the more complex double perovskite family. The ability to postulate compositions drives the synthetic chemist to pursue the discovery of new materials and the investigation of their physical properties.

The preparation of specific double perovskite compositions is commonly approached via the traditional solid-state synthetic method which, of course, requires a target composition. For example, the powder preparation, structural characterization, and magnetic properties of the double perovskite, La_2MgIrO_6 were previously reported [2,9]. Interestingly, until now, there have not been any reports on the incorporation of lanthanide metals with ionic radii smaller than lanthanum into the Ln_2MgIrO_6 type double perovskites. Our initial attempts to prepare the title compounds by traditional solid state techniques yielded unfavorable results where the desired phases formed with impurity phases, such as the defect fluorites with the general formula Ln_3IrO_7 (Ln=Pr, Nd, Sm, Eu) [10] or with an unreacted starting reagent, such as magnesium oxide, in the product. Where traditional solid state synthetic techniques encounter limits, another method, materials discovery by crystal growth using hydroxide fluxes [11], has been established as an excellent

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approach for preparing compounds with targeted compositions and structure types that can be rationalized by radius ratio rules and new compounds with unique compositions and structures [12,13].

Our attempt to circumvent some of the limitations of traditional solid-state synthetic techniques using hydroxide flux reactions has resulted in the preparation of high quality single crystals of the title compounds. The crystal growth, structural characterization, and magnetic properties of Pr_2MgIrO_6, Nd_2MgIrO_6, Sm_2MgIrO_6, Eu_2MgIrO_6, and Gd_2MgIrO_6 are reported herein.

2. Experimental

2.1. Crystal growth

For all compounds, the lanthanide sesquioxides, Ln_2O_3 (Nd, Sm, Eu, Gd), (Alfa Aesar, 99.99%) were fired at 1000 °C for 12 h prior to the reactions. Pr_6O_{11} (Alfa Aesar, 99.9%) was converted to Pr_2O_3 by heating Pr_6O_{11} at 1000 °C for 24 h under a reducing 5% H_2 atmosphere. KOH (Fisher Scientific, A.C.S Reagent Grade, 99.9%), iridium powder (Engelhard, 99.99%) and MgO (Alfa Aesar, 99.998%) were used as received. Single crystals of Ln_2MgIrO_6 were grown from a high temperature melt of potassium hydroxide. Ln_2O_3 (Pr, Nd, Sm, Eu, Gd) (0.5 mmol), MgO (1 mmol), Ir (0.5 mmol), and KOH (4 g) were loaded into sealed silver tubes and heated in a box furnace to a temperature of 700 °C at 10 °C/min, held for 24 h at 700 °C, slow cooled to 600 °C at 0.2 °C/min and then allowed to cool to room temperature by turning off the furnace. The black crystals were removed from the flux matrix by dissolving the flux in water aided by sonication. The crystals were finally extracted by vacuum filtration.

2.2. Scanning electron microscopy

Single crystals of Ln_2MgIrO_6 (Ln=Pr, Nd, Sm–Gd) were analyzed by scanning electron microscopy using an FEI Quanta SEM instrument utilized in the low vacuum mode. Energy dispersive spectroscopy verified the presence of Mg, Ir, O and the respective lanthanide element, and within the detection limits of the instrument, confirmed the absence of extraneous elements, such as potassium and silver. A scanning electron micrograph of a single crystal of Sm_2MgIrO_6 is shown in Fig. 1.

2.3. Structural determination

For the structure determination of Ln_2MgIrO_6 (Ln=Pr, Nd, Sm, Eu, Gd), X-ray diffraction intensity data were measured at 294(2) K using a Bruker SMART APEX diffractometer (Mo$K\alpha$ radiation, λ=0.71073 Å) [14]. Each data collection covered a minimum of 99.1% of reciprocal space to $2\theta_{max}$=75°, with a minimum reflection redundancy to $2\theta_{max}$ of 4.3. The raw area detector data frames were processed with SAINT+ [14]. An absorption correction based on the redundancy of equivalent reflections was applied to the data with SADABS [14]. Reported unit cell parameters were determined by least-squares refinement of all reflections from the data sets with $I > 10\sigma(I)$. Full-matrix least-squares refinement against F^2 and difference Fourier calculations and were performed with SHELXTL [14].

The compounds adopt the monoclinic double perovskite structure type, in the space group $P2_1/n$. Refinement of this structural model converged rapidly. The β angle is near 90° in all cases; however, the pattern of systematic absences in the intensity data was not consistent with any orthorhombic space group. The asymmetric unit in $P2_1/n$ consists of three metal and three oxygen atom positions: Ln1 is on a general position (Wyckoff symbol 4*e*), Mg1 is on an inversion center (Wyckoff symbol 2*a*), Ir1 is on an inversion center (Wyckoff symbol 2*b*) and oxygen atoms O1–O3 are on general positions. Atoms were generally refined with anisotropic displacement parameters. The exception to this is the magnesium atom, which could be refined anisotropically only for Ln=Nd and Gd. Mg1 was refined isotropically for Ln=Pr, Sm and Eu. The reason for this is not clear, but likely due to the combined effects of moderate crystallinity and twinning in the specific systems. Trial refinements of site occupancy parameters showed no significant deviations from unity occupancy for the lanthanide or iridium atoms in any case. Because of the metrical similarity of the lattice to orthorhombic, all compounds except Ln=Gd were twinned to emulate orthorhombic symmetry. These refinements included the twin law [100/0-10/00-1] (two-fold rotation around [100]). The refined major twin fractions are Pr, 0.515(3); Nd, 0.796(3); Sm, 0.540(3); Eu, 0.656(3). Trial twin refinement of the Ln=Gd dataset gave a major twin fraction within experimental error of 1.0, with no improvement in *R*-values. The largest residual difference map peak/hole for the compounds are Pr: $+3.22/-2.82\,e^-/Å^3$, located 0.71 Å from Ir1/0.39 Å from Pr1; Nd: $+4.09/-3.54\,e^-/Å^3$, located 0.58 Å from Ir1/0.56 Å from Nd1; Sm: $+3.82/-2.68\,e^-/Å^3$, located 0.69 Å from Ir1/0.41 Å from Sm1; Eu: $+2.71/-2.69\,e^-/Å^3$, located 0.74 Å from Ir1/1.10 Å from Eu1; Gd: $+4.01/-2.80\,e^-/Å^3$, located 0.63 Å/0.57 Å from Ir1, respectively. Relevant crystallographic data for the five materials are presented in Table 1, atomic positions are given in Table 2, and selected interatomic distances and bond angles are listed in Table 3.

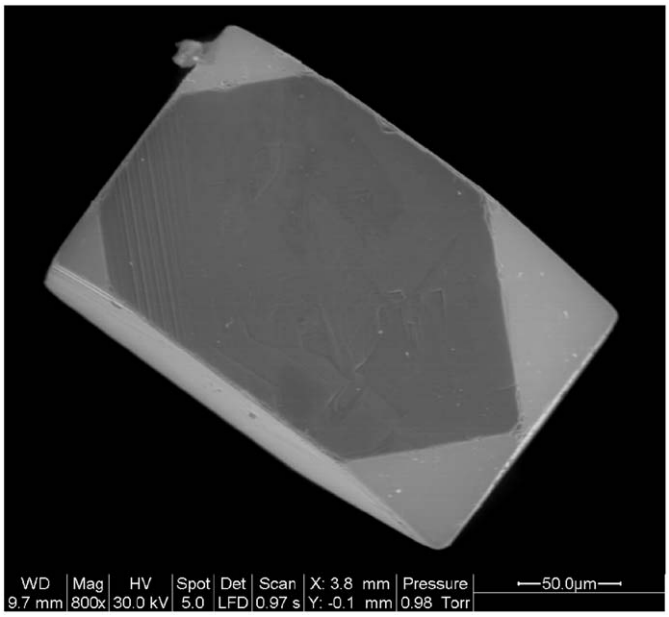

Fig. 1. An environmental scanning electron microscope image of a Sm_2MgIrO_6 single crystal.

2.4. Magnetic measurements

The magnetic susceptibility measurements of loose single crystals of Pr_2MgIrO_6, Nd_2MgIrO_6, Sm_2MgIrO_6, Eu_2MgIrO_6, and Gd_2MgIrO_6 were performed using a Quantum Design MPMS XL SQUID magnetometer. The samples were measured under both zero field cooled (ZFC) and field cooled (FC) conditions in applied fields of 1 and 10 kG over the temperature range of $5\,K \le T \le 300\,K$. The samples were contained in gel capsules suspended in a plastic straw for immersion into the SQUID.