Journal of Solid State Chemistry 220 (2014) 28–31

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Synthesis, crystal structure and magnetic properties of a new *B*-site ordered double perovskite Sr_2CuIrO_6

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A R T I C L E I N F O

Article history:
Received 15 July 2014
Received in revised form
7 August 2014
Accepted 11 August 2014
Available online 19 August 2014

Keywords:
Double perovskite oxide
High-pressure synthesis
Jahn–Teller distortion
Magnetic properties

A B S T R A C T

Here we synthesize and characterize a new double-perovskite oxide Sr_2CuIrO_6. The synthesis requires the use of high oxygen pressure to stabilize the VI oxidation state of iridium. The compound has a tetragonally-distorted crystal structure due to the Jahn–Teller active Cu^{II} ion, and a high degree of *B*-site cation order. Magnetic transition is apparent at 15 K, but the zero-field-cooled and field-cooled susceptibilities diverge below this temperature. The high degree of cation order would exclude the possibility of a typical spin-glass, indicating that the divergence is probably due to a frustration of the magnetic interactions between Cu and Ir, with a high frustration factor of $f \approx 25$.

1. Introduction

The *B*-site ordered double-perovskite copper oxides of the composition $A_2CuB''O_6$, where *A* is Sr or Ba and B'' is a hexavalent cation, Mo, Te, W, Os or U, have over the years gained some interest due to their particular crystal structure features [1–18]. The compounds are ideal in the sense that they possess practically complete *B*-site cation order, but the crystal structure is tetragonally distorted ($c/a\sqrt{2} \approx 1.08–1.11$) due to a cooperative Jahn–Teller distortion of the $CuO_{6/2}$ octahedra of divalent copper, with the long Cu–O_c bonds ordered along the *c* axis and the short Cu–O_{ab} bonds remaining in the *ab* plane. However, what make these compounds special are their magnetic properties varying depending on the electron configuration of the B'' cation.

When B'' is a diamagnetic ion, i.e. Mo, Te or W, the $A_2CuB''O_6$ compounds show a quasi-low-dimensional magnetic behavior, characterized with a broad maximum in the magnetic susceptibility [1,8–10,16,17]. Because of the cooperative JT distortion, the half-filled Cu d_{x2-y2} orbitals are ordered into the *ab* plane, whereas the orbitals pointing towards the *c* direction (d_{z2}, d_{yz}, and d_{zx}) are fully filled. This results in relatively strong magnetic interactions within the *ab* plane, but weaker interactions in the *c* direction, making the magnetic interactions quasi-two-dimensional. On the other hand, Ba_2CuUO_6 with the diamagnetic U^{VI} ion has been reported either as a quasi-low-dimensional compound [4,5] or as a typical antiferromagnet [6,7]. In Ba_2CuOsO_6 the magnetic susceptibility is also notably broadened [18], whereas in Sr_2CuOsO_6 only very weak broadening appears to be present [14]. Interestingly, the B''=Os compounds show a divergence between zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities at low temperatures, which is not seen in the other $A_2CuB''O_6$ compounds. Divergence of the ZFC and FC susceptibilities has been found for several perovskites of the $A_2B'B''O_6$ composition, and is often related to a spin-glass-type behavior [19–27]. These compounds however typically have a low degree of *B*-site cation order, which causes the spin-glass-type magnetic frustration. In contrast, the A_2CuOsO_6 compounds show practically complete cation order, which would exclude a typical spin-glass behavior.

It is thus evident that the B''-site cation has a great effect on the magnetic properties of the $A_2CuB''O_6$ compounds, and it is of interest to find more examples of this double-perovskite series. In this work, we synthesize and characterize a novel compound Sr_2CuIrO_6 with Ir^{VI} at the B'' site. Seven $A_2B'IrO_6$ compounds with *A*=Sr or Ba and B'=Mg, Ca, Sr, Ni or Zn have been previously described in the literature [28–33]. All of these compounds require a synthesis under high oxygen pressure in order to stabilize the VI oxidation state of iridium. We thus use high pressure synthesis for the preparation of Sr_2CuIrO_6, characterize its crystal structure and magnetic properties and compare it to the other members of the $A_2CuB''O_6$ double-perovskite family.

2. Experimental

The Sr_2CuIrO_6 samples were prepared through a high-pressure (HP) synthesis route. A thoroughly ground mixture of $SrCO_3$, CuO

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http://dx.doi.org/10.1016/j.jssc.2014.08.008
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and IrO_2 powders was first calcined at 900 °C for 12 h in flowing O_2. The resultant multi-phase powder mixture was then used as a precursor for the HP synthesis. The powder was sealed in a gold capsule together with $KClO_3$ as an external oxygen source (twice the stoichiometric amount) and treated in a cubic-anvil HP apparatus (Riken-Seiki) at ca. 4 GPa and 900 °C for 60 min. The KCl residue left over from the decomposition of $KClO_3$ was washed away with methanol in an ultrasonic bath (as washing with water appeared to cause slight degradation in the samples, detected from broadening of the x-ray diffraction peak bases).

Phase purity and crystal-structure details of the samples were examined by x-ray powder diffraction (XRD; PANanalytical X'Pert PRO MPD Alpha-1) with Cu$K_{\alpha 1}$ radiation. The XRD patterns were analysed with a Rietveld refinement program FULLPROF [34]. DC magnetic susceptibility was measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design: MPMS-XL5). The measurements were performed under a magnetic field of 1 kOe in both field-cooled (FC) and zero-field-cooled (ZFC) modes. The measurement temperature range was from 5 to 300 K. Isothermal magnetization was measured from −50 kOe to 50 kOe at 5 K.

3. Results and discussion

Synthesis of Sr_2CuIrO_6 was found not to work at ambient pressure in air or under flowing oxygen. Instead, various mixtures of phases such as $Sr_4CuIr_2O_9$ and CuO_2, or Sr_3CuIrO_6, IrO_2 and CuO_2 were formed, with only tetravalent Ir. However, nearly phase pure black polycrystalline Sr_2CuIrO_6 could be obtained through the high-pressure synthesis route using $KClO_3$ as an oxygen generator. In the HP samples, a tiny amount (~2% by Rietveld refinement) of unreacted CuO impurity could be detected. Additionally, other very weak reflections from impurity phases were seen, which could not be identified.

Rietveld refinement of the XRD pattern was done using a tetragonal space group $I4/m$ (#87). This space group is commonly found in the Jahn–Teller distorted rock-salt ordered $A_2CuB''O_6$ double perovskites [1–18]. The Rietveld refinement result is shown in Fig. 1. During the refinement, a slight anisotropic peak broadening was noticed. To remedy this, we tested refinements of anisotropic size or strain parameters, and both the methods were found to successfully model the broadening. However, we could not definitely verify which phenomenon was the cause for the broadening, due to the relatively small effect. For the final refinement, anisotropic strain was used. This is reasonable in that the compound was synthesized under high pressure, which could well cause some remnant strain in the samples. The final refinement indicated that the strain was higher along the c axis, by about 75% compared to the a or b axes.

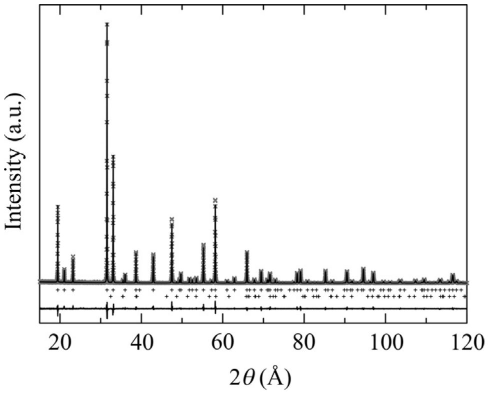

Fig. 1. Rietveld refinement results for Sr_2CuIrO_6. The tick marks show the positions of reflections for Sr_2CuIrO_6 (top row) and a CuO impurity (bottom row).

The Rietveld refinement results for Sr_2CuIrO_6 are gathered in Table 1. The compound was found to be JT distorted, with a tetragonal distortion of $c/a\sqrt{}\approx 1.10$. The B-site cation degree of order $S=2g_B-1$, where g_B is the occupancy of a B-site cation on its correct site, was found to be 0.90, showing a small amount of B-site cation disorder. The Cu–O_{ab} and Cu–O_c distances were found to be ~1.95 Å and ~2.24 Å, respectively. The Cu–O bond lengths and the degree of JT distortion are similar to the other $A_2CuB''O_6$ compounds, indicating the Cu^{II} formal oxidation state in this compound. The $IrO_{6/2}$ octahedra were also found to be slightly elongated along the c axis, with Ir–O_{ab} and Ir–O_c distances of ~1.94 Å and ~1.97 Å, respectively. However, JT distortion is not expected for the $t_{2g}^3e_g^0$ state of Ir^{VI}. The difference in the bond lengths is quite small and probably below the detection limit of laboratory XRD. On the other hand, this slight distortion could be caused by the small amount of B-site cation disorder, with some JT distorted Cu at the Ir site appearing to elongate the Ir–O_c bonds. The ionic radius of Ir was determined as ~0.55 Å, similar to Ir^{VI} radius found in other $A_2B'IrO_6$ compounds [28,31–33].

Magnetic susceptibility of Sr_2CuIrO_6 is shown in Fig. 2 as a function of temperature. The ZFC curve shows a magnetic transition at around 15 K. This transition appears antiferromagnetic, but there is a notable divergence between the ZFC and FC curves below the transition temperature. There is also a small rise in the

Table 1
Rietveld refinement results for Sr_2CuIrO_6. Space group $I4/m$ (#87). Sr is at site (0, 0.5, 0.25), Cu at (0, 0, 0.5), Ir at (0, 0, 0), O_{ab} at (x, y, 0) and O_c at (0, 0, z).

a (Å)	5.40717(4)
c (Å)	8.41320(7)
$c/a\sqrt{2}$	1.10
V (Å^3)	245.980(3)
O_{ab} x	0.202(1)
O_{ab} y	0.297(1)
O_c z	0.2341(9)
Cu–O_{ab} (Å)	1.951(6)
Cu–O_c (Å)	2.237(8)
Ir–O_{ab} (Å)	1.940(6)
Ir–O_c (Å)	1.970(8)
Cu–O_{ab}–W (°)	158.5(2)
g_B	0.951(2)
S	0.90
CuO (%)	2.09
R_p (%)	13.2
R_{wp} (%)	17.2
R_{Bragg} (%)	4.18
χ^2	2.61

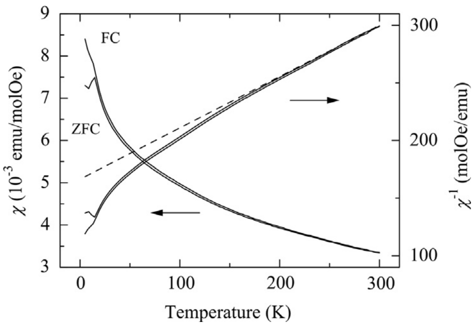

Fig. 2. Magnetic susceptibility and inverse of magnetic susceptibility as a function of temperature for Sr_2CuIrO_6. The dashed line shows the high-temperature fit to the Curie-Weiss law.