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Hydrothermal synthesis and magnetic properties of a new phase of $SrCo_2(PO_4)_2$

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ABSTRACT

A new compound β-$SrCo_2(PO_4)_2$ was successfully synthesized under mild hydrothermal condition. The structure consists of two types of edge-shared [Co_2O_{10}] dimers which connect to each other via corner sharing to form two-dimensional (2D) CoO-layers. Further, these layers are linked by PO_4 tetrahedra and Sr^{2+} cations, leading to a three-dimensional (3D) framework. As evidenced by the results of susceptibility and magnetization measurements, this compound displays a long-range antiferromagnetic (AFM) ordering at 27 K. Moreover, the results of thermal analyses reveal that a small quantity of β phase would be converted to α form after heating.

1. Introduction

Transition-metal phosphates with a formula of $AM_2(PO_4)_2$ (A = Sr, Ba, Pb; M = Mn, Fe, Ni, Co, Cu) have attracted considerable interest because they display enormous structural diversity and various magnetic properties. Analysis of coordination and linkage of M atoms is very important to understand crystal structures and magnetic behaviors. In general, magnetic M^{2+} ion coordinates with oxygen atoms to form a [MO_n] (n = 4, 5 and 6) polyhedron, which further results in 0D cluster, 1D chain and 2D layer by corner- or edge-sharing. Therefore, different magnetic properties are obviously observed in the system. For example, the Cu^{2+} ions in $BaCu_2(PO_4)_2$ constitute isolated zigzag chains and magnetic susceptibility exhibits a abroad maximum around 65 K [1,2], while two isotypic compounds $SrCu_2(PO_4)_2$ [3,4] and $PbCu_2(PO_4)_2$ [5,6] are built up from corner-sharing [Cu_2O_8] units showing a spin singlet state with a spin gap. Among three honeycomb lattice compounds $BaNi_2(PO_4)_2$, $BaFe_2(PO_4)_2$ and γ-$BaCo_2(PO_4)_2$, the Ni-compound is an antiferromagnet with a Neel temperature at 24 K [7,8]. The Fe-compound has a structural transition at 140 K (*R*-3 → *P*-1) and a ferromagnetic (FM) ordering at 65.5 K accompanying the rare re-entrant structural *P*-1 → *R*-3 transition [9,10]. Additionally, it is found that this compound displays the amusing exsolution of Fe^{2+} ions [11–13]. Up to now, there are three certain phases for Co-compound. The high temperature γ phase is a helimagnet with FM chains below 3.8 K [14–16]. The low temperature monoclinic α form is constructed from zigzag chains shows a canting AFM below 17 K and transforms to trigonal β phase at 973 K containing isolated CoO_4 tetrahedra without reports of magnetism [17].$SrFe_2(PO_4)_2$ consists of 2D layers based on linear Fe2—Fe1—Fe1—Fe2 tetrameric clusters and undergoes structural phase transition at 11.3 K and canting AFM at 7.0 K [18,19]. $SrMn_2(PO_4)_2$ contains 2D MnO-layers constructed from Mn_4 and Mn_8 clusters, and no results of magnetic behaviors are published [20]. To compare the interesting characters of iso-formular compounds $AM_2(PO_4)_2$ mentioned above, the synthesis, structural parameters and magnetic properties are summarized in Table 1.

In our previous work, we reported the synthesis of $SrCo_2(PO_4)_2$ (named α-$SrCo_2(PO_4)_2$) by a high temperature solid state reaction [21]. To obtain new compounds in this system, we adopt a hydrothermal method which has been widely used to produce new materials. In this article, we have successfully synthesized a new phase of $SrCo_2(PO_4)_2$ (named β-$SrCo_2(PO_4)_2$) under a mild hydrothermal condition. The 3D framework of β-$SrCo_2(PO_4)_2$, which is different from the α phase with a structural characterization of four spin units [22], contains 2D CoO-layers involving two types of

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Table 1
The synthesis, crystal structures and magnetic properties of $AM_2(PO_4)_2$ family which are abbreviated to AM_2.

Compound abbreviation	Synthesis method	Space group	*a* (Å) *α* (°)	*b* (Å) *β* (°)	*c* (Å) *γ* (°)	d_{M-M} (Å) ∠M–O–M (°)	Topology of M polyhedra	J/κ_B (K)	Structural and magnetic transition	Ref.
$BaCu_2$	SSR	*P*-1	9.226 106.76	9.271 101.69	10.516 115.70	3.474 to 3.736 121.00 to 124.90	Zigzag chain	−51.6 and −49.5	SRO at 65 K, no LRO above 2 K	[1,2]
$SrCu_2$	SSR	*Pccn*	7.942 90	15.369 90	10.370 90	3.256 96.85	Dimer	−41.2 and −29.5	spin-singlet with a gap of 63 K, no LRO above 0.45 K	[3,4]
$PbCu_2$	SSR	*Pccn*	8.038 90	15.465 90	10.368 90	3.273 101.33	Dimer	−48.5 and −43.3	spin-singlet with a gap of 43 K, no LRO above 0.45 K	[5,6]
α-$BaCo_2$	SSR	$P2_1/a$	9.211 90	5.004 92.74	8.085 90	3.568 122.66	Zigzag chain	–	transform to β-$BaCo_2$ at 1173 K, canting AFM transitions at 17 K	[17]
β-$BaCo_2$	Transition from α phase	*P-3*	5.223 90	5.223 92	8.261 120	–	Isolated	–	–	[17]
γ-$BaCo_2$	SSR or HTM	*R-3*	4.855 90	4.855 90	23.215 120	2.808 84.02	Honeycomb	20, 0 and −8	helical magnetic structure with FM chains at 3.8 K	[15,16]
α-$SrCo_2$	SSR	*P*-1	5.014 118.04	8.639 75.09	9.691 86.90	3.058 and 3.409 99.72 and 117.54	Four spin cluster	–	LRO AFM at 23 K	[21,22]
β-$SrCo_2$	HTM	*P*-1	5.503 110.23	6.703 101.15	9.238 98.29	3.049 to 4.015 91.64 to 123.19	2D layer	–	LRO AFM at 27 K	This work
$BaNi_2$	SSR	*R-3*	4.811 90	4.811 90	23.302 120	2.780 84.96	Honeycomb	−18, −7.2 and −9.9	LRO AFM at 24 K	[7,8]
$SrNi_2$	SSR	*P*-1	5.468 110.58	6.667 100.87	9.156 98.01	2.993 to 4.005 92.05 to 124.27	2D layer	–	two AFM orderings at 23 and 10 K, spin-flop at 2 K with $H_c = 4$ T	[25,26]
$BaFe_2$	HTM	*R-3*	4.873 90	4.873 90	23.368 120	2.818 82.95	Honeycomb	16.84, 1.43 and 3.76	structural transition at 140 K, FM and another structural transition at 65.5 K	[9,10]
$SrFe_2$	SSR	$P2_1/c$	9.354 90	6.838 109.51	10.519 90	2.971 to 4.056 78.39 to 114.48	2D layer	–	structural transition at 11.4 K, canting AFM transitions at 7.4 K	[18,19]
$SrMn_2$	SSR	*P*-1	8.860 124.27	9.054 90.23	10.260 90.26	3.293 to 3.698 95.19 to 115.26	2D layer	–	–	[20]

SSR: solid state reaction; HTM: hydrothermal; LRO: long-range ordering; SRO: short-range ordering.

$[Co_2O_{10}]$ dimers formed from $Co(1)O_6$ and $Co(2)O_6$ octahedra via edge sharing. These layers are separated by PO_4 tetrahedra and Sr^{2+} cations. Magnetic susceptibility and magnetization demonstrate the β form exhibits the typical feature of antiferromagnet with a magnetic ordering at 27 K, a little higher than that of α phase ($T_N = 23$ K) [21]. Thermal analyses testify that a small number of β phases would be transformed to α phase after thermal treatment for 5 h.

2. Experimental

2.1. Materials and methods

All reagents were used as received without further purification except α-$Co_2P_2O_7$ which was synthesized by solid state reaction according to Ref. [23]. Single crystal of β-$SrCo_2(PO_4)_2$ was prepared through a facile hydrothermal synthesis route. A mixture of α-$Co_2P_2O_7$ (0.0584 g, 0.2 mmol), $Sr(NO_3)_2$ (0.0846 g, 0.4 mmol) and 5 mL H_2O was stirred for 10 min in air. The obtained mixture was then transferred into a 28 mL Teflon-lined autoclave and heated at 230 °C in an oven for 120 h. The autoclave was cooled down to room temperature at a rate of 0.1 °C/min, and purple rhombus-shaped crystals of β-$SrCo_2(PO_4)_2$ were isolated, washed with distilled water and dried in air at 60 °C.

2.2. Measurements

Powder X-ray diffraction (PXRD) date was carried out using a Rigaku MiniFlex-II X-ray Powder Diffractometer in the range of 5–65° with the scanning rate of 5°/min at room temperature. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were measured on a NETZSCH 449C thermal analyzer instrument with the temperature ranging from 30 to 1000 °C under N_2 atmosphere using a heat rate of 10 °C/min. The magnetic susceptibility was recorded on a Quantum Design SQUID MPMS-XL magnetometer from 2 to 300 K at applied field of 0.1 T. Isothermal magnetization at 2 K was performed by a Quantum Design PPMS instrument from 0 to 8 T.

2.3. X-ray crystallography

Single crystal X-ray diffraction intensity data of the titled compound were collected at 293 K using Rigaku Mecurry CCD area detector diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by the full-matrix least-squares technique on F^2 using the program SHELXTL [24]. All atoms were found from difference Fourier maps and refined anisotropically. The detailed crystal data and refinement parameters for β-$SrCo_2(PO_4)_2$