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Synthesis, structure and magnetic properties of new γ-$Ba(CoV_{1-x}P_xO_4)_2$ x = 0.4–0.5

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ABSTRACT

The phase composition of the system $BaCo_2(VO_4)_2$–$Ba(CoPO_4)_2$ has been studied. At room temperature two miscibility gaps have been detected, with the formation of substitutional solid solutions $Ba(CoV_{1-x}P_xO_4)_2$ for x = 0.4–0.5 basing on the γ-BCPO structure type. An increase in the vanadium cation concentration leads to the stabilization of the rhombohedral crystal lattice. The crystallographic characteristics of two new phosphate - vanadates $Ba(CoV_{0.5}P_{0.5}O_4)_2$ and $Ba(CoV_{0.6}P_{0.4}O_4)_2$ isostructural to γ-BCPO have been obtained, their crystal structures have been described, and their magnetic properties have been analyzed. It was shown that in α-BCPO, as distinct from other examined phases, a three-dimensional ferromagnetic ordering characterized by a wide hysteresis loop takes place at low temperatures. The enhanced values of the magnetic moment in the paramagnetic phase $BaCo_2(VO_4)_2$ and solid solutions based on γ-BCPO are attributed to the peculiarities of the crystal environment.

1. Introduction

The layered compounds of the general formula $Ba(MXO_4)_2$ (M = Co, Cu, Fe, Mn, Ni; X = As, P, V) attract much attention due to the variety of properties caused by the peculiarities of the layered structure [1–3]. For example, in $Ba(CoAsO_4)_2$, a quasi-two-dimensional XY system is realized, in which cobalt ions form a frustrated magnetic structure, featuring almost ferromagentic chains capable of twisting without large energy inputs and T_N ~ 5.4 K [3]. For $Ba(NiVO_4)_2$ having the same crystal structure, an antiferromagnetic ordering at T_N ~ 50 K and a Kosterlitz-Thouless transition at T_{KT} ~ 43 K were found [1]. Quite recently, quasi-one-dimensional spin systems were found in vanadates of transition metals $AM_2V_2O_8$, where A = Ba, Sr, Pb; M = Cu, Co, Ni [4–7]. It was shown that $BaCo_2(VO_4)_2$ and vanadates $BaMg_2V_2O_8$ and $SrCo_2V_2O_8$ [4,8–11] possess exceptional microwave properties. Besides, vanadium-containing compounds are also considered as low-sintered ceramics, and some of them are compatible with silver electrodes [12–15]. Moreover, the basic compounds $Ba(MXO_4)_2$ represent a large platform of new structure types since they can adapt their polymorphic modifications to synthesis conditions and annealing history. The parent compounds in the $BaCo_2(VO_4)_2$–$Ba(CoPO_4)_2$ system differ considerably in chemical composition, physical properties and crystal structure. In the lattice of $BaCo_2(VO_4)_2$ the CoO_6 and VO_4 tetrahedra form a three-dimensional network with the tunnels where barium atoms are placed [16]. While in barium and cobalt phosphates, the mutual orientation of polyhedras is more diverse.

The phase diagram and magnetic properties of the layered compound $Ba(CoPO_4)_2$ are investigated R. David et al. [1]. Preparation of a high-temperature phase $Ba(CoPO_4)_2$ (here and in after referred to as γ-modification), γ-$Ba(CoPO_4)_2$, is complicated. It is more easy to produce a low-temperature modification (α-$Ba(CoPO_4)_2$). The low-temperature α-form is transformed into several polymorphic modifications, which also have a layered structure. Three reversible transitions take place at 773, 893 and 993 K, which makes it possible to determine the following types of polymorphic modifications: $\alpha \rightarrow \alpha^I \rightarrow \alpha^{II} \rightarrow \beta$ (Fig. 1).

The structures of first three α-modifications are interconnected, whereas β-$Ba(CoPO_4)_2$ (trigonal structure) is isomorphic to $CaZn_2P_2O_8$ and $BaAl_2Si_2O_8$. All of them are layered, but differ significantly from the high-temperature γ-modifications in structure and way of stacking of the layers (Fig. 2), and therefore these compounds are not polytypes. The authors [1] report the refined data on the crystal structure of α-BCPO and attribute it to monoclinic system (Fig. 2). The compound has a 2D structure consisting of $(CoPO_4)$ chains separated by barium cations.

Isovalent substitution of cations, including their displacement in the oxygen polyhedra of anions, provides the possibility to create novel materials. In the $BaCo_2(VO_4)_2$–$Ba(CoPO_4)_2$ system, both new double

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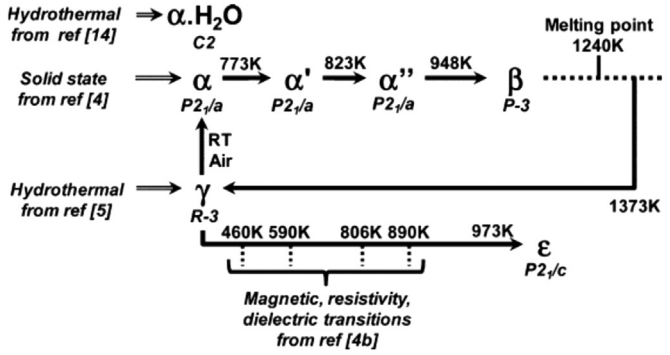

Fig. 1. Phase relationships of $Ba(CoPO_4)_2$ according to [1].

phosphate - vanadates, whose crystal structure will be different from that of initial compounds, and primary solid solutions are expected to form. The authors supposed that the substitution of vanadium cations for phosphorus cations in the crystal lattice of $Ba(CoPO_4)_2$ may increase the stability of γ-modification.

In this work we present the results of investigation of the system $BaCo_2(VO_4)_2$ – $Ba(CoPO_4)_2$, the crystal structure and magnetic characteristics of γ-$Ba(CoP_{1-x}V_xO_4)_2$, x = 0.4 and 0.5, $BaCo_2(VO_4)_2$ and α-$Ba(CoPO_4)_2$.

2. Experimental

2.1. Sample preparation

$BaCO_3$, $(NH_4)_2HPO_4$, $Co(NO_3)_2{\cdot}6H_2O$ and V_2O_5 (99.5–99.9%) were used as initial reagents for synthesis. The synthesis of samples was carried out for obtaining 0.02 g-mole barium cobalt phosphate - vanadates. Barium carbonate was dissolved in a solution of citric acid taken in the ratio of 3 mol $C_6H_8O_7{\cdot}H_2O$ per 1 mol $BaCO_3$; after its dissolution, cobalt nitrate was added to the solution (solution 1). Solution 2 was prepared separately by dissolving a sample of V_2O_5 in a solution of citric acid taken in the ratio of 2 mol $C_6H_8O_7{\cdot}H_2O$ per 1 mol V_2O_5 while stirring and heating. After dissolution of V_2O_5, a calculated amount of $(NH_4)_2HPO_4$ was added to solution 2. Solutions 1 were poured to solution 2 and heated in a glass jar.

In the process of heating and water removal, a gel was formed, which turned into a xerogel during drying. Further heating of the xerogel initiated a redox reaction typical of solution combustion synthesis (SCS) at excessive content of reducer relative to stoichiometry [17]. On completing SCS, a loose black powder of $Ba(CoV_{1-x}P_xO_4)_2$, x = 0–1, precursor remained in the jar. The precursor was ground in an agate mortar, placed in an aluminum crucible, and subjected to stepwise annealing in a muffle furnace. The maximal annealing temperature of samples with dominating vanadium content did not exceed 850 °C, and the samples with prevailing phosphorus concentration were annealed at 900–920 °C. The total synthesis time at maximal temperatures was 50–60 h.

2.2. Characterization

The purity of the synthesized product was checked using X-ray powder diffraction (XRD). The XRD patterns were collected at room temperature on a STADI-P (Stoe) diffractometer in transmission geometry with a linear mini-PSD detector in the 2θ range 5–120° with a step of 0.02°. Focused $CuK\alpha_1$ incident beam was obtained using curved germanium (111) monochromator. Polycrystalline silicon (a = 5.43075 (5) Å) was used as external standard. The possible impurity phases were checked by comparing their XRD patterns with those in the PDF2 database [18]. The crystal structure refinement was carried out with the GSAS program suite using the XRD data [19,20]. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) = xL(2\theta) + (1-x)G(2\theta)$ (where L and G are the Lorentzian and Gaussian part, respectively). The angular dependence of the peak width was described by the relation $(FWHM)^2 = Utg^2\theta + Vtg\theta + W$, where FWHM is the full line width at half maximum. The background level was described by a combination of thirty-six-order Chebyshev polynomials. The absorption correction function for a flat plate sample in transmission geometry was applied.

Differential thermal analysis (DTA) was performed using a Setsys Evolution thermal analyzer (Setaram) in air at a temperature scan rate of 10°/min in the temperature range 20–1050 °C, with alumina as a standard.

The magnetic properties of all synthesized samples were measured using a VSM-5T CRYOGENIC vibratory magnetometer in the temperature range 2–300 K in fields to 5 T.

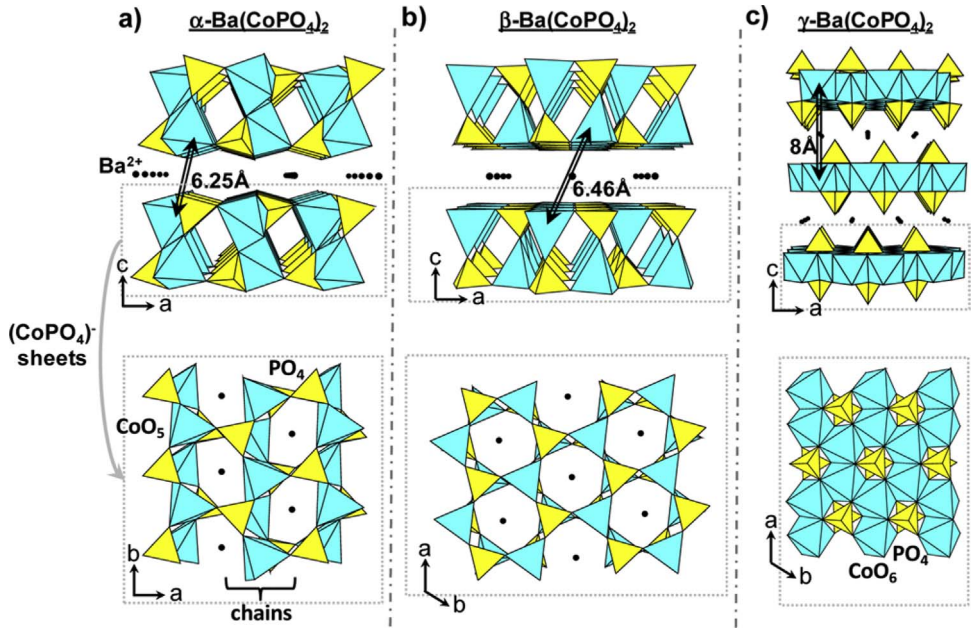

Fig. 2. Description of the 2D structure of (a) α-$Ba(CoPO_4)_2$, (b) β-$Ba(CoPO_4)_2$, and γ-$Ba(CoPO_4)_2$ [1].