

SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Interaction between Samarium and Cobalt Carbonates in Aqueous Medium

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Abstract—The $\text{Sm}_2(\text{CO}_3)_3\text{--CoCO}_3\text{--H}_2\text{O}$ system was studied using isothermal crystallization (295 K). The compounds $\text{Sm}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, $\text{Sm}_2\text{Co}_5(\text{CO}_3)_8 \cdot 30\text{H}_2\text{O}$, $\text{Sm}_2\text{Co}_7(\text{CO}_3)_{10} \cdot 40\text{H}_2\text{O}$, $\text{Sm}_2\text{Co}_{17}(\text{CO}_3)_{20} \cdot 54\text{H}_2\text{O}$, and $\text{Co}(\text{CO}_3)_{0.7}(\text{OH})_{0.6} \cdot 2\text{H}_2\text{O}$, as well as solid solutions based on samarium carbonate and samarium cobalt double carbonates were found in the system.

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Manufacturing permanent magnets containing rare-earth metals with high magnetic characteristics include alloying metal components in vacuum induction or electric arc furnaces, dispersion of the melts by hydrogen or mechanical treatment in modern milling and crushing equipment, followed by orientation of the powders obtained in magnetic field, their compaction, and sintering [1–3]. Alternatively, powders are prepared in laboratory and industrial practice by reduction reducing diffusion process based on the calcium thermal reduction of mixtures of oxides, hydroxides, chlorides, carbonates, and other compounds of rare-earth metals and cobalt in a hydrogen atmosphere. This method makes it possible to prepare powders suitable for manufacturing permanent magnets avoiding the stages of melting and mechanical grinding [2].

However, to obtain homogeneous mixture of various powdered salts (precursors for production of permanent magnets), it is necessary to have information on the regions of their cocrystallization and coexistence. In this connection, the aim of this work was to determine the crystallization fields of samarium cobalt carbonates in aqueous medium.

EXPERIMENTAL

Starting reagents. The starting reagents were commercially available chemically pure Na_2CO_3 , metallic samarium (99.83% of purity), and metallic cobalt (99.99%). Solutions of SmCl_3 and CoCl_2 were prepared by dissolving of corresponding metals in a 12% HCl solution taken in stoichiometric amounts.

Procedure. Due to low water solubilities of samarium and cobalt carbonates, the title system was studied using crystallization of carbonates in the course of the reaction of samarium and cobalt chlorides with sodium carbonate under stoichiometric conditions. Equilibrium at 295 ± 1 K was reached after 3 to 25 h.

In the first set of experiments, a Na_2CO_3 solution was added to SmCl_3 and CoCl_2 solutions; in the second set, SmCl_3 and CoCl_2 solutions were added to a Na_2CO_3 solution. We either varied the amount of Na_2CO_3 added and determined the ratio between Sm and Co in the products of crystallization, or varied this ratio at a constant Na_2CO_3 concentration. In both cases, the concentrations of the solutions of the initial compounds were calculated so that to provide a fixed concentration of the by-product NaCl (~ 0.19 mol/L).

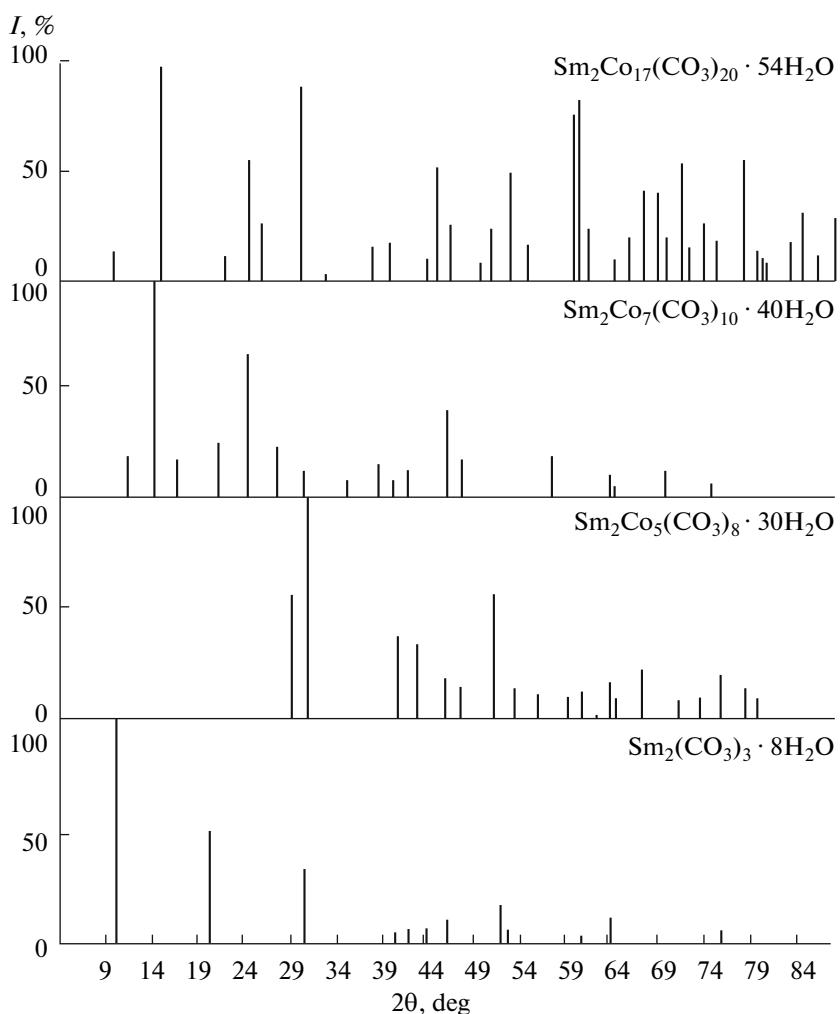
Analyses. Chemical analysis of bottom phases for samarium, cobalt, chlorine, sodium, and CO_2 was car-

Table 1. Compositions of eutonic points in the $\text{Sm}_2(\text{CO}_3)_3\text{--CoCO}_3\text{--H}_2\text{O}$ system

Point no.	Relative contents of the components of the system, wt %		Composition of eutonic points
	$\text{Sm}_2(\text{CO}_3)_3$	CoCO_3	
1	98.0	2.0	$\text{Sm}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ + solid solutions
2	50.0	50.0	Solid solutions + $\text{Sm}_2\text{Co}_5(\text{CO}_3)_8 \cdot 30\text{H}_2\text{O}$
3	38.0	62.0	$\text{Sm}_2\text{Co}_5(\text{CO}_3)_8 \cdot 30\text{H}_2\text{O}$ + $\text{Sm}_2\text{Co}_7(\text{CO}_3)_{10} \cdot 40\text{H}_2\text{O}$
4	31.0	69.0	$\text{Sm}_2\text{Co}_7(\text{CO}_3)_{10} \cdot 40\text{H}_2\text{O}$ + $\text{Sm}_2\text{Co}_{17}(\text{CO}_3)_{20} \cdot 54\text{H}_2\text{O}$
5	17.0	83.0	$\text{Sm}_2\text{Co}_{17}(\text{CO}_3)_{20} \cdot 54\text{H}_2\text{O}$ + $\text{Co}(\text{CO}_3)_{0.7}(\text{OH})_{0.6} \cdot x\text{H}_2\text{O}$

Table 2. Interactions in the $\text{Sm}_2(\text{CO}_3)_3-\text{CoCO}_3-\text{H}_2\text{O}$ system

Point no. in the Schreinemakers ray	Composition of the bottom phase, wt %		Ratio, wt %		Solid phase
	$\text{Sm}_2(\text{CO}_3)_3$	CoCO_3	$\text{Sm}_2(\text{CO}_3)_3$	CoCO_3	
	67.12	0.0	100.0	0.0	$\text{Sm}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$
1	4.99	0.34	98.4	1.6	Solid solutions
2	8.83	0.44			
1	5.01	0.35	97.3	2.7	The same
2	75.03	1.27			
1	6.02	0.38	90.1	9.9	"
2	38.56	4.08			
1	7.14	0.81	84.1	15.9	"
2	13.94	2.14			
1	12.72	3.58	82.8	17.2	"
2	14.77	3.98			
1	20.82	7.68	73.2	26.8	"
2	47.84	19.00			
1	6.72	1.82	69.9	30.1	"
2	11.39	3.88			
1	3.38	2.50	63.3	36.7	"
2	37.71	22.08			
1	4.64	3.78	56.2	43.8	"
2	31.62	24.68			
1	9.24	9.72	43.6	56.4	$\text{Sm}_2\text{Co}_5(\text{CO}_3)_8 \cdot 30\text{H}_2\text{O}$
2	18.03	21.67			
1	3.92	3.92	44.0	56.0	The same
2	7.52	8.60			
1	3.41	5.74	44.8	55.2	"
2	25.31	31.95			
1	5.28	8.89	45.2	54.8	"
2	25.52	32.05			
1	12.84	20.12	36.6	63.4	$\text{Sm}_2\text{Co}_7(\text{CO}_3)_{10} \cdot 40\text{H}_2\text{O}$
2	23.64	39.75			
1	3.39	5.70	37.2	62.8	The same
2	5.38	8.96			
1	1.22	5.53	37.8	62.2	"
2	1.33	5.70			
1	2.58	8.83	16.9	83.1	$\text{Sm}_2\text{Co}_{17}(\text{CO}_3)_{20} \cdot 54\text{H}_2\text{O}$
2	13.84	67.27			
1	1.35	5.76	17.6	82.4	The same
2	1.92	8.48			
1	1.20	5.56	19.1	80.9	"
2	1.94	8.55			
1	2.83	10.10	19.5	80.5	"
2	13.62	55.55			
1	7.94	18.45	25.5	74.5	"
2	14.92	40.67			
1	1.36	2.52	13.3	86.7	$\text{Sm}_2\text{Co}_{17}(\text{CO}_3)_{20} \cdot 54\text{H}_2\text{O}$
2	3.34	18.48			+ $\text{Co}(\text{CO}_3)_{0.7}(\text{OH})_{0.6} \cdot 2\text{H}_2\text{O}$
3	6.50	37.83			
1	1.10	17.80	6.5	93.5	The same
2	1.82	27.88			
	0.0	28.5	0.0	100.0	$\text{Co}(\text{CO}_3)_{0.7}(\text{OH})_{0.6} \cdot 2\text{H}_2\text{O}$



X-ray line diagrams of the compounds formed in the $\text{Sm}_2(\text{CO}_3)_3-\text{CaCO}_3-\text{H}_2\text{O}$ system.

ried out by routine procedures.. Solid phases were also analyzed for carbon and water.

The solid phase composition was found by the Schreinemakers method [4]. For this purpose, two or three samples of a bottom phase were analyzed, and the resulting compositions were connected by Schreinemakers rays in the Schreinemakers diagram. The intersection of these rays gave the composition of the solid phase.

X-ray diffraction studies of carbonates in the $\text{Sm}_2(\text{CO}_3)_3-\text{CoCO}_3-\text{H}_2\text{O}$ system were carried out on a computer-interfaced ADP-1 diffractometer ($\text{Cr}K_\alpha$ radiation). X-ray diffraction patterns were recorded for 35 min in the presence of the mother liquor.

RESULTS AND DISCUSSION

Six crystallization fields were found in the system $\text{Sm}_2(\text{CO}_3)_3-\text{CoCO}_3-\text{H}_2\text{O}$ (Tables 1, 2). Compound $\text{Sm}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ crystallizes in the range of up to 2.0 wt % CoCO_3 . In the CoCO_3 concentration range

from 2.0 to 50.0 wt %, solid solutions based on $\text{Sm}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Sm}_2\text{Co}_5(\text{CO}_3)_8 \cdot 30\text{H}_2\text{O}$ crystallize. In the range from 50.0 to 62.0 wt % CoCO_3 , complex compound $\text{Sm}_2\text{Co}_5(\text{CO}_3)_8 \cdot 30\text{H}_2\text{O}$ exists. In the range of 62.0–69.0 wt % CoCO_3 , double carbonate $\text{Sm}_2\text{Co}_7(\text{CO}_3)_{10} \cdot 40\text{H}_2\text{O}$ exists; and crystallization of complex $\text{Sm}_2\text{Co}_{17}(\text{CO}_3)_{20} \cdot x\text{H}_2\text{O}$ ($x = 54 \pm 5.4$) is observed in the range of 69.0–83.0 wt %.

In the region with high CoCO_3 concentrations (≥ 83 wt %), the system has not been studied, because the effect of hydrolysis is so essential that the system is no longer ternary, and the basic cobalt carbonate $\text{Co}(\text{CO}_3)_{0.7}(\text{OH})_{0.6} \cdot x\text{H}_2\text{O}$ ($x = 2.2 \pm 0.5$) appears in the bottom phase. The composition was determined by chemical analysis of the product of the reaction of CoCl_2 with Na_2CO_3 under stoichiometric conditions.

Therefore, three double carbonates, a samarium carbonate, and a basic cobalt carbonate were found to exist in the $\text{Sm}_2(\text{CO}_3)_3-\text{CoCO}_3-\text{H}_2\text{O}$ system. The chemical analysis results are compiled in Table 3. Once being separated from the mother liquor, the car-

Table 3. Chemical analysis of the carbonates found in the Sm₂(CO₃)₃–CoCO₃–H₂O system

Compound	Found, wt %				Calcd., wt %			
	Sm	Co	C	H ₂ O	Sm	Co	C	H ₂ O
Sm ₂ (CO ₃) ₃ ·8H ₂ O	46.9	—	6.0	22.2	48.12	—	5.76	23.07
Sm ₂ Co ₅ (CO ₃) ₈ ·30H ₂ O	18.1	18.1	5.9	34.3	18.60	18.23	5.94	33.45
Sm ₂ Co ₇ (CO ₃) ₁₀ ·40H ₂ O	14.8	19.7	6.0	35.5	14.78	20.28	5.89	35.44
Sm ₂ Co ₁₇ (CO ₃) ₂₀ ·54H ₂ O	8.6	30.4	6.0	31.0	8.65	28.82	6.90	28.00
Co(CO ₃) _{0.7} (OH) _{0.6} ·2H ₂ O	—	39.0	5.6	26.4*	—	40.04	5.70	24.48

* Found by difference.

bonates gradually lose part of their water. Double carbonates Sm₂Co₅(CO₃)₈·30H₂O, Sm₂Co₇(CO₃)₁₀·40H₂O, and Sm₂Co₁₇(CO₃)₂₀·54H₂O can be used to manufacture permanent magnets.

Analysis of the X-ray powder diffraction data of the crystallization products in the system shows the absence of possible admixtures: Na₂CO₃, NaCl, Sm₂O(CO₃)₂·xH₂O, Sm(OH)CO₃, CoCO₃, basic cobalt carbonate, as well as crystal hydrate of samarium carbonate Sm₂(CO₃)₃·2.85H₂O and a complex of samarium carbonate with sodium carbonate. Thus, the X-ray line diagrams presented in the figure correspond to the individual compounds.

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