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HIGH-PRESSURE AND HIGH-TEMPERATURE SYNTHESIS OF $LaCo_2$

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ABSTRACT

High pressures and high temperatures were used to synthesize previously unknown $LaCo_2$. This compound has the cubic $MgCu_2$-type structure with a lattice parameter of 7.449 A. Attempts to prepare $EuCo_2$ and $LaCo_3$ were not successful.

Introduction

Other investigators (1-6) have studied the cobalt-lanthanide systems under atmospheric pressure and high temperatures. In the LCo_2 and LCo_3 (L= lanthanide) series, these compounds usually crystallize in the face-centered cubic $MgCu_2$-type and hexagonal $PuNi_3$-type structures respectively. In the LCo_2 series, some of the investigators (1,5,6) reported that attempts to synthesize $LaCo_2$ were unsuccessful. One set of investigators (5) reported that attempts to synthesize $EuCo_2$ were also unsuccessful. In the LCo_3 series, no researcher has reported the synthesis of $LaCo_3$ and Buschow (1) observed that any attempt to synthesize $LaCo_3$ was not successful.

In our previous publication (7) it was shown that high-pressure and high-temperature techniques were useful in synthesizing the previously unknown LFe_2 compounds (L= Pr,Nd,Yb). Since a similar size relationship exists in both the LCo_2 and LFe_2 (L= lanthanide) series, we applied high pressures and temperatures in an attempt to synthesize the unknown compounds $LaCo_2$, $EuCo_2$ and $LaCo_3$.

Experimental

The tetrahedral press developed by Hall (8,9) was used to generate the high pressures and temperatures needed for this work. Complete information about sample geometry and calibration procedures are described elsewhere (10). Briefly, the tetrahedral samples consisted of a graphite-tube heater with a boron nitride liner surrounding the reactants. Molybdenum tabs were used for the electrical leads from the anvil

face to the graphite. The tetrahedrons were painted with a slurry of methanol and ferric oxide and allowed to dry at room temperature, The pressures used ranged from a minimum of 10 kbar to a maximum of 65 kbar. The temperatures ranged from 1050° C to 1350° C. The reaction times for best results averaged about 2-5 minutes.

Information about the metals used in this study can be found in Table 1.

Table I
Information about Metals used

Metal	Size	Purity	Source	Preparation
La	-100 mesh powder (under oil)	99.9%	Research Organic/Inorganic Chemical Corp. Sun Valley, California	Seived through 100-mesh sieve
Eu	Ingot (under oil)	99.6%	Research Chemicals Inc. Phoenix, Arizona	Filed under argon and not sieved*
Co	-200 mesh powder	99.8%	Matheson, Coleman and Bell, Norwood, Ohio	used as received

*The Eu was an estimated 80-100 mesh powder after filing.

The powders were hand mixed in the desired stoichiometric ratio. To avoid oxide formation, the mixed powders were kept in air tight vials in a desiccator.

The reacted samples were crushed and X-rayed without further preparation on a General Electric XRD-5 powder diffraction unit with chromium radiation (λ =2.29092 A). The samples were mounted on a 143.2 mm Debye-Scherrer camera by means of a 0.5 mm glass capillary. The Nelson-Riley extrapolation method (11) was used to correct for the absorption error in determining the lattice constants.

Results

Of the three compounds under investigation, only $LaCo_2$ was successfully synthesized. This compound crystallized in the cubic $MgCu_2$-type structure with a lattice parameter of 7.449 A and a standard deviation of 0.005 A. The calculated and observed d values for $LaCo_2$ are shown in Table 2.

Table 2
Intensities and d Values

hkl	Intensity	d calc	d obs
2 2 0	6	2.634	2.625
3 3 1	10	2.246	2.240
2 2 2	2	2.150	2.045
4 2 2	3	1.521	1.518
5 1 1	4	1.434	1.433
4 4 0	4	1.317	1.317

The minimum pressure required to synthesize $LaCo_2$ was about 14-18 kbar. Any run at a pressure greater than this minimum pressure yielded the product. In the X-ray spectrum of this compound, no oxide contamination was observed and no lines due to the reactants were present. There were some minor, unidentified lines which do not correspond to any known La-Co compound.

The X-ray spectra of the 1:2 (mole ratio) Eu-Co runs did not show any reactants but no $MgCu_2$-type lines were present either. In the 1:3 La-Co runs, some 1:5 compound was observed in the X-ray even though we had started with a 1:3 ratio. There were some extra lines also which were not accounted for by the 1:5 structure alone. However, we did not observe any lines in the X-ray films characteristic of the common 1:3 type.

The cubic $LaCo_2$ is not stable at high temperature under one atmosphere pressure. We placed some of the $LaCo_2$ in a tube furnace for one hour at a temperature about 600° C. (Ar gas was passed over the sample during the heating process.) When the X-ray spectrum of the cooled sample was examined, there was no evidence of any $MgCu_2$-type structure.

Discussion

In a work examining the cobalt-lanthanide compounds, Buschow (1) observed that both LCo_2 and LCo_3 were present in all lanthanide systems except when L= La. Buschow stated that both the 1:2 and 1:3 structures can be derived from the basic 1:5 $CaCu_5$-type structure, In deriving the 1:3 La-Co compound from the 1:5 compound, he stated that a La atom must be substituted for a Co atom in alternating $LaCo_5$ cells. This substitution is also accompanied by a slight layer shift which favors the substitution. However, if the cubic Laves phase, $LaCo_2$, is derived from the $LaCo_5$ structure, a La atom must be substituted for a Co atom in every unit cell without a layer shift. Consequently, it would appear that the stability of $LaCo_2$ would be more dependent on the lanthanide to non-lanthanide radius ratio than would the stability of $LaCo_3$ (1). It would then seem likely that if high pressure was necessary to synthesize either the 1:2 or 1:3 compound, the 1:3 would be more easily formed.

From our high pressure work, we observed that this may not necessarily be the case. We could easily synthesize $LaCo_2$ but were not able to synthesize $LaCo_3$ at any pressure. It is likely, however, that factors other than just a favorable size relationship are important in the formation of $LaCo_3$. It is also conceivable that under high pressure conditions, this compound may crystallize in a structure other than the common $PuNi_3$-type.

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