Influence of the lanthanide on the composition and structure of hydrated $Ln$ chromates

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Abstract. The effect of the $Ln^{3+}$ cation type on the composition and structure of a wide range of hydrated lanthanide chromates ($Ln =$ La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Yb, Y) has been studied. It was found that hydrated $Ln$ chromates can be divided into several groups in terms of their composition and structure. The synthesized chromates of light lanthanides crystallize into heptahydrates $[Ln_2(CrO_4)_3(H_2O)_5] \cdot 2H_2O$ ($Ln =$ La, Pr, Nd, Sm) and tetrahydrate $Eu_2(CrO_4)_3 \cdot 4H_2O$ with a monoclinic structure (sp. gr. $P2_1/c$). The chromates of heavy lanthanides ($Ln =$ Gd, Dy, Ho, Yb, Y) remain X-ray amorphous.

1. Introduction

Different chromates $Ln_2(CrO_4)_3$, $LnCrO_4$ and chromites $LnCrO_3$ ($Ln =$ La-Lu) represent a large group of compounds lanthanide elements and $d$-elements of the VIB subgroup. This group of complex oxides includes an unusually large number of polymorphic modifications formed by changing the lanthanide type, temperature, and pressure. [1, 2]. The uniqueness of this group also lies in the fact that even with the same $Ln$ type, it is possible to carry out phase transformations in the series $Ln_2(Cr^{6+}O_4)_3 \rightarrow LnCr^{5+}O_4 \rightarrow LnCr^{3+}O_3$, associated with a change in the oxidation state of chromium cations from (+6) to (+3) [1, 2]. These materials are suitable for exploiting their fundamental physical and chemical properties as well as for technological applications, mainly due to a large number of ground states and properties observed, such as multiferroicity, high-temperature superconductivity, colossal magnetoresistance, and many others [3].

The aim of this work was to study the effect of $Ln^{3+}$ cation type on the composition and structure of a wide range of hydrated lanthanide chromates ($Ln =$ La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Yb, Y) using a set of physicochemical methods of analysis.

2. Experimental

Lanthanide chromate powders were synthesized by precipitation of aqueous solutions of $Ln$ nitrates $Ln(NO_3)_3$ with potassium chromate $K_2CrO_4$. The reaction suspensions were kept under vigorous stir-
ring for 1 h and then were filtered. The resulting precipitates were washed several times with acetone and dried in the air at room temperature.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements on Vista-PRO spectrometer (Varian Inc.) were used to determine the concentration of elements in the analyzed samples. Simultaneous thermal analysis (STA), involving thermogravimetry (TG) and differential scanning calorimetry (DSC), was carried out by using SDT Q 600 (TA Instruments) analyzer. Phase/composition identification was made by X-ray diffraction analysis on Rigaku MiniFlex 600 diffractometer with CoKα-radiation ($\lambda = 1.79 \text{ Å}$). The detailed structural information was obtained by the synchrotron s-XRD study at the X-ray Structural Analysis beamline (XSA) of the Kurchatov synchrotron radiation source (NRC Kurchatov Institute, Moscow, Russia) (2.5 GeV storage ring with an average current of 100 mA), using monochromatic radiation with a wavelength of 0.74 Å [4]. The full profile analysis was carried out by the Rietveld method using JANA2006 software [5]. The Fourier transform infrared (FT-IR) spectra were recorded on Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific Inc.), equipped with a single reflection diamond module (ATR). IR spectra were collected in the range of wavenumber 400 – 4000 cm$^{-1}$ with a 4 cm$^{-1}$ resolution. The Raman spectra were collected using the inVia Qontor confocal Raman microscope (Renishaw) at $\lambda = 532 \text{ nm}$ in the wavenumber range 50 – 2600 cm$^{-1}$ with a spectral resolution of 1 cm$^{-1}$.

3. Results and Discussion

According to ICP-AES data, all synthesized $Ln$ chromate powders can be conditionally divided into two groups: light lanthanides ($Ln = \text{La, Pr, Nd, Sm, Eu}$) with a chemical composition corresponding to the atomic ratio $Ln : Cr = 1 : 1.5$ close to stoichiometric formula $Ln_2(\text{CrO}_4)_3$, and heavy lanthanides and yttrium ($Ln = \text{Gd, Dy, Ho, Yb, Y}$) with the chemical composition $Ln : Cr \leq 1 : 1$ (Table 1). This is apparently associated with the formation of insoluble deposits of basic chromates with the general formula $Ln(\text{OH})\text{CrO}_4 \cdot xLn(\text{OH})_3$.

| $Ln$ type | Chemical composition, wt. % | Atomic ratio $Ln$/Cr | Mass loss (from TG at 450$^\circ$C), % | $n\text{H}_2\text{O}$ (from TG) |
|----------|-----------------------------|-----------------------|-------------------------------------|-------------------------------|
| La       | 33.25                       | 18.23                 | 0.39                                | 1 : 1.49                      | 16.75                          | 7                              |
| Pr       | 32.51                       | 18.61                 | 0.53                                | 1 : 1.55                      | 17.07                          | 7                              |
| Nd       | 36.73                       | 18.20                 | 0.72                                | 1 : 1.37                      | 16.72                          | 7                              |
| Sm       | 32.87                       | 17.83                 | 1.16                                | 1 : 1.57                      | 16.12                          | 7                              |
| Eu       | 37.62                       | 18.82                 | 3.09                                | 1 : 1.46                      | 11.04                          | 4                              |
| Gd       | 43.55                       | 14.36                 | 2.54                                | 1 : 1.00                      | 15.29                          | -                              |
| Dy       | 42.75                       | 12.82                 | 2.24                                | 1 : 0.94                      | 16.41                          | -                              |
| Ho       | 47.66                       | 12.18                 | 1.97                                | 1 : 0.81                      | 16.26                          | -                              |
| Yb       | 51.58                       | 10.49                 | 1.31                                | 1 : 0.68                      | 16.47                          | -                              |
| Y        | 33.28                       | 15.21                 | 2.70                                | 1 : 0.78                      | 21.32                          | -                              |

*Presence of low potassium content indicates a small amount of double chromates $KLn(\text{CrO}_4)_2$ in the samples.

The obtained STA data showed that all synthesized hydrated $Ln$ chromates can be also divided into several groups. The first group is the light lanthanide ($Ln = \text{La, Pr, Nd, Sm}$) chromates. For these compounds, several features can be clearly distinguished on the TG curves, accompanied by several endo- and exothermic processes on the DSC curves (Fig. 1a). The calculations (taking into account the data of the ICP-AES) showed that this group corresponds to heptahydrates with the composition $Ln_2(\text{CrO}_4)_3 \cdot 7\text{H}_2\text{O}$ ($Ln = \text{La, Pr, Nd, Sm}$) (Table 1). The results obtained are in good agreement with the literature data [6, 7]. A characteristic feature of the STA curves for the above compounds is the presence of several stages of dehydration, a distinct exothermic peak in the region of 400 – 450 $^\circ$C on the DSC curves and a plateau in the temperature region of 400 – 550 $^\circ$C on the TG curves (Fig. 1a). The second group is only Eu chromate, which, despite the ratio Eu/Cr = 1.46, corresponds to the crystal hydrate $Eu_2(\text{CrO}_4)_3 \cdot 4\text{H}_2\text{O}$ (Table 1). And the third group is the heavy lanthanide chromates ($Ln =$
Gd, Dy, Ho, Yb, and Y), the thermal behavior of which differs significantly from those mentioned above. Namely, the DSC data of these compounds do not show an exothermic peak at 430 – 460 °C, as well as there is no plateau at 400 – 550 °C on the TG curves (Fig. 1b).

According to XRD data, all synthesized chromates can be also divided into two groups: light lanthanides (\(Ln = \text{La, Pr, Nd, Sm, Eu}\)) with a crystal structure (Fig.2a), and heavy lanthanides and yttrium (\(Ln = \text{Gd, Dy, Ho, Yb, Y}\)), which are X-ray amorphous (Fig.2b). As can be seen from Fig. 2a, \(Ln (Ln = \text{La, Pr, Nd, Sm})\) chromates are isostructural, while the crystal structure of Eu chromate (as well as the amount of \(\text{H}_2\text{O}\) molecules - see Table 1) differs from the other light \(Ln\) chromates.

It was found that hydrated light \(Ln (Ln = \text{La, Pr, Nd, Sm})\) chromates have a monoclinic structure (space group \(P2_1/c\)). Detailed information on the parameters of the atomic-crystal structure and metal-oxygen bond lengths for this group of compounds are presented in Table 2. The obtained results are in good agreement with the literature data [6-8]. As can be seen from Table 2, a decrease in the lattice parameters and unit cell volume of hydrated \(Ln\) chromates were observed with a decrease in the \(Ln^{3+}\) cation radii ongoing from La to Sm. The performed analysis has shown that Eu chromate also had a monoclinic structure, but with different lattice parameters and structural basis (sp. gr. \(P2_1/c(1)\)).

Additional information on the local structure of the anionic sublattice of the synthesized chromates was obtained by vibrational spectroscopy (IR and Raman). Four vibrational modes of the free \(\text{CrO}_4^{2-}\) anion (tetrahedron, \(T_d\) symmetry): \(v_1(A_1)\) at 846 cm\(^{-1}\) (symmetric-stretching), \(v_2(E)\) at 349 cm\(^{-1}\) (symmetric bending), \(v_3(F_2)\) at 890 cm\(^{-1}\) (antisymmetric-stretching), and \(v_4(F_2)\) at 368 cm\(^{-1}\) (antisymmetric-bending) are active to Raman and only \(v_3(F_2)\) and \(v_4(F_2)\) – for IR spectroscopy [9, 10].
Table 2. The results of XRD Rietveld refinement for light $Ln$ chromates ($Ln$ = La, Pr, Nd, Sm, Eu)

| $Ln$ type | Space group | La | Pr | Nd | Sm | Eu |
|-----------|-------------|----|----|----|----|----|
|           | $P2_1/c$    | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/c(1)$ |
| $a$, Å    | 8.1895(2)   | 8.0970(3) | 8.0705(5) | 8.0218(3) | 17.9778(12) |
| $b$, Å    | 19.2871(7)  | 19.1366(8) | 19.0436(14) | 18.8860(7) | 10.6490(6)  |
| $c$, Å    | 13.3049(4)  | 13.1955(5) | 13.1982(9) | 13.1794(6) | 16.2551(9)  |
| $\beta$, ° | 127.169(3)  | 127.046(2) | 127.111(4) | 127.114(3) | 116.457(3)  |
| $V_{cell}$, Å$^3$ | 1674.6(9) | 1623.3(7) | 1617.6(2) | 1592.2(2) | 2786.1(3) |
| CSR, nm   | 200(20)    | 490(60)   | 470(80)   | 270(20)   | 750(120)    |
| $\varepsilon$, % | 13(7)*$10^{-5}$ | 17(11)*$10^{-5}$ | 39(17)*$10^{-5}$ | 60(18)*$10^{-5}$ | 8(7)*$10^{-5}$ |
| $d(Ln_1-O)$, Å | 2.580 | 2.629 | 2.525 | 2.526 | - |
| $d(Ln_2-O)$, Å | 2.695 | 2.564 | 2.531 | 2.572 | - |
| $d(Cr_1-O)$, Å | 1.638 | 1.602 | 1.786 | 1.538 | - |
| $d(Cr_2-O)$, Å | 1.569 | 1.565 | 1.632 | 1.550 | - |
| $d(Cr_3-O)$, Å | 1.569 | 1.523 | 1.486 | 1.743 | - |
| $R_p$     | 7.12       | 6.93      | 10.55     | 6.55      | 4.75 |
| $R_{wp}$  | 11.17      | 10.27     | 10.24     | 9.85      | 9.48 |

Common to all IR spectra of hydrated $Ln$ chromates (Fig. 3) is the presence of several characteristic features in the region of 3200 – 3600 cm$^{-1}$ and near 1600 cm$^{-1}$, corresponding to stretching $\nu$(H-OH) and bending $\delta$(H-O-H) vibrations of hydrogen-bonded OH-group of water molecules, respectively. The observed splitting of these stretching and bending vibrations indicated the inequality of water molecules in the structure of hydrated light $Ln$ chromates. At the same time, some water molecules are connected more rigidly, which was confirmed by the presence in the IR spectra of the librational vibrations of water molecules $\rho$(H$_2$O) at 650 cm$^{-1}$ [11]. Thus, the structure of heptahydrates chromate $Ln_2$($CrO_4$)$_3$·7H$_2$O ($Ln$ = La, Pr, Nd, Sm) is more correctly represented in the form $[Ln_2(CrO_4)_3(H_2O)_3]·2H_2O$. This is a good agreement with the TG results (Fig. 1a) and literature data [6, 7, 11]. The three most intense bands observed in hydrated light $Ln$ chromates in the region of 900 cm$^{-1}$ (Fig. 3) correspond to the components of the triple degenerate stretching vibration $\nu_1(F_2)$ of CrO$_2^2-$ anion [11]. The absorption bands in the range 825–845 cm$^{-1}$ correspond to the symmetric vibration $\nu_1(A_1)$, the splitting of which can be caused by different coordination of CrO$_4$ groups [11]. This is in good agreement with the results of XRD measurements (Table 2). Low-frequency bands in the region of 450 cm$^{-1}$ probably correspond to $Ln$-O vibrations [11].

![Fig. 3. IR spectra of hydrated $Ln$ chromates](image1)

![Fig. 4. Raman spectra of hydrated $Ln$ chromates](image2)

As can be seen from Fig. 3, the presence of a fine structure (several absorption bands) inside each of the indicated regions gradually became less pronounced on going from La to Sm. The transition to heavy $Ln$ chromates led to an almost complete absence of the fine structure of the IR spectra (Fig. 3),
which, apparently, can be associated with the X-ray amorphous structure of heavy Ln chromates. It is interesting to note that the IR spectra of Eu chromate and other heavy Ln chromates are quite similar despite the differences in their structural ordering.

There are nine vibrational modes in monoclinic crocoite (PbCrO$_4$), all of which are Raman and IR-active [12]. To the best of the knowledge of the authors, no Raman spectroscopy of the Ln chromates has been reported. It was found that all synthesized Ln chromates were very sensitive to laser heating. Therefore, all measurements of the Raman spectra were carried out at a low laser power (≤ 1 mW) and exposure time (≤ 1 s). For light Ln chromates the observed Raman modes are related to the stretching (750 – 950 cm$^{-1}$) and bending (300 – 450 cm$^{-1}$) vibration modes of the Cr-O bonds with a broad empty gap in the range 500 – 700 cm$^{-1}$ (Fig. 4). Some vibrations in the low wavenumber range (< 200 cm$^{-1}$) related to lattice modes [12]. The Raman spectrum of monoclinic La$_2$(CrO$_4$)$_3$.7H$_2$O showed the lattice modes at 84, 98, 157, 196, and the Raman at 329, 370, 385 (shoulder), 433, 820, 854 (shoulder), 872, 907, 926 and 958 cm$^{-1}$ (Fig. 4). The band at 872 cm$^{-1}$ was the most intense and was assigned to the $\nu_5(F_2)$ CrO$_4^{2-}$ stretching vibration. The Raman spectra of other Ln light chromates were similar. At the same time the Raman spectra of amorphous heavy Ln chromates contained only several broad modes (Fig. 4). It should be noted that there is an analogy between the Raman spectra of Ln chromates and similar Ln molybdates reported in [13].

4. Conclusion
A comprehensive study of the effect of Ln$^{3+}$ cation type on the composition and structure of hydrated lanthanide chromates ($Ln =$ La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Yb, Y), prepared by precipitation, was carried out. The analysis was performed using a combination of s-XRD, Raman and IR spectroscopy, supplemented by STA and ICP-AES. It was found that hydrated Ln chromates can be divided into several groups according to their composition and structure. Namely, crystalline heptahydrates of light lanthanides [Ln$_2$(CrO$_4$)$_3$(H$_2$O)$_5$].2H$_2$O ($Ln =$ La, Pr, Nd, Sm) and tetrahydrate Eu$_2$(CrO$_4$)$_3$.4H$_2$O, with a monoclinic structure (sp. gr. P2$_1$/c), as well as X-ray amorphous chromates of heavy lanthanides ($Ln =$ Gd, Dy, Ho, Yb, Y). The XRD results correlated well with IR and Raman spectroscopy. They provided information on the local structure of the compounds. It was concluded that one of the basic structural units of Ln chromates were the CrO$_4$ tetrahedra.

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