Observation of polytypism among the hydroxysalts of Ni(II) and Co(II)

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ABSTRACT

Layered hydroxysalts derive their crystal structure from mineral brucite. Nickel and cobalt based hydroxysalts with the composition $M_3(OH)_4(NO_3)_2$ crystallize in trigonal crystal system. On careful examination of the PXRD patterns, it is found that $Ni_3(OH)_4(NO_3)_2$ crystallizes in hexagonal crystal system while $Co_3(OH)_4(NO_3)_2$ crystallizes in rhombohedral crystal system. This clearly demonstrates that the crystal structures in layered hydroxysalts are mainly dictated by the nature of the cation occupying the preferential site within the layer.

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Layered metal hydroxides, layered hydroxysalts and layered double hydroxides have drawn considerable attention of materials chemists due to its potential application in catalysis, electrochemistry, as precursors to nanoparticulate oxides, ion exchange reactions, etc. [1–6]. Divalent metal hydroxides, layered hydroxysalts and layered double hydroxides derive their structure from brucite, a mineral form of $Mg(OH)_2$ [7–9]. The structure of layered hydroxysalts comprise of a stacking of hydroxyl deficient positively charged layers with the composition $[M(OH)_{2-x}]^{x+}$ (M = metal ion). The structure incorporates anions ($A^{n-} = Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}$) in the interlayer region for charge neutrality with the resulting composition $[M(OH)_{2-x}](A^{n-})_{x/n}$. The commonly observed values of 'x' for hydroxysalts are 0.5, 0.67 and 1.0, respectively [10,11]. The structure of hydroxyl-rich phases with composition $M_3(OH)_4A_2$, and $M_2(OH)_3A$ crystallize in mineral brucite [12]. In case of nickel, cadmium and magnesium based hydroxysalts, the metal ion occupies octahedral interstitial site, while in zinc and cobalt based hydroxysalts, the metal ion occupies both octahedral and tetrahedral interstices within the layer. The interlamellar distance in these layered hydroxysalts are determined by the size of the interlayer anion and commonly varies from 6.9 to 9.2 Å (for Mg, Ni, Co, Zn and Cd systems) [13,14]. We have recently reported $Co_3(OH)_4(NO_3)_2$ phase in which all the Co^{2+} ions occupy octahedral sites within in brucite-like layers [15]. Rajamathi and Kamath have reported the basic salt of nickel with the composition $Ni_3(OH)_4(NO_3)_2$ [16]. In all the above compounds, the layers are stacked along the c-crystallographic direction and depending on the arrangement of stacking of layers with respect to each other, differ-

ent type of polytypes can be formed [17]. In contrast to the polytypism investigated in layered double hydroxides, layered metal chalcogenides and carbides, polytypism in layered hydroxysalts is less studied [7,18]. In this paper we have examined the polytypism in layered hydroxysalts especially in nickel hydroxynitrate and cobalt hydroxynitrate.

The basic salts of Ni(II) and Co(II) were synthesized by following the procedure reported in literature [6,19]. The urea hydrolysis of Ni(II) salt was carried out at 160 °C and Co(II) salt at 150 °C.

The products were characterized by powder X-ray diffraction (PXRD) using a Philips powder X-ray diffractometer (Cu K α source, $\lambda = 1.5418$ Å). Data were collected at a scan rate of $2\theta^\circ \text{ min}^{-1}$ with 2θ steps of 0.05° . Infrared spectra were recorded using a Nicolet Model Impact 400D FTIR spectrometer (KBr pellets, 4 cm^{-1} resolution). Thermogravimetry was carried out using a Mettler Toledo Model 851e TG/SDTA system (heating rate $10^\circ \text{ C min}^{-1}$). All the samples were heated to 800 °C for 2 h and the weight loss was accounted. All the samples were subjected to wet chemical analysis as described elsewhere [15].

DIFFaX simulations studies were carried out using DIFFaX code. The details about the PXRD simulations have been explicitly defined in the literature [15].

The PXRD pattern of the products obtained from nickel nitrate and cobalt nitrate melts are shown in Fig. 1a and c, respectively. The chemical composition of these two samples were found to be $Ni_3(OH)_4(NO_3)_2$ and $Co_3(OH)_4(NO_3)_2$, respectively. Thermogravimetric analysis of nickel hydroxynitrate and cobalt hydroxynitrate samples shows weight loss of 38.8% and 33.2%, respectively. Wet chemical analysis of cobalt hydroxynitrate sample shows the absence of Co^{3+} content in the sample. Infrared spectra of nickel hydroxynitrate and cobalt hydroxynitrate samples shows sharp

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Fig. 1. The PXRD patterns of (a) observed nickel hydroxynitrate, (b) DIFFaX simulated nickel hydroxynitrate, (c) observed cobalt hydroxynitrate and (d) DIFFaX simulated cobalt hydroxynitrate samples.

band in the higher wave number region (3625 cm^{-1} and 3606 cm^{-1}) due to stretching vibration of OH groups. A weak band at $3300\text{--}3310\text{ cm}^{-1}$ arises due to hydrogen bonded OH groups of adsorbed water molecules. In the mid wave number ($1000\text{--}1600\text{ cm}^{-1}$) we observe strong absorption bands at ν_1 : 1310 cm^{-1} ; ν_3 : 990 cm^{-1} and ν_4 : 1503 cm^{-1} and have been assigned to the strongly bound nitrate group while the fourth (ν_2 : 1385 cm^{-1}) arises due to the interaction of the sample with the KBr in the pellet. The large splitting $\Delta\nu = 193\text{ cm}^{-1}$, between the ν_4 and ν_1 vibrational modes of the nitrate ion in the infrared spectrum of nickel hydroxynitrate reveals that one of the oxygen atoms of the nitrate group is directly coordinated to the metal ion [20,21].

In case of hexagonal layered compounds, we observe Bragg reflections due to (i) $00l$ planes; (ii) $hk0$ planes; (iii) $h0l/OkI$ planes and (iv) hkl planes [22]. The PXRD pattern of both the samples display two successive reflections at 6.98 Å and 3.46 Å , respectively could be indexed to $00l$ planes. The $hk0$ reflections provide information about the a -parameter of the samples. The metal to metal distance (a -parameter) within the layer for nickel hydroxynitrate and cobalt hydroxynitrate are 3.13 Å and 3.18 Å , respectively. The differences in these values arise due to the variation in the metal to oxygen bonding within the layer. If we carefully examine the PXRD patterns of these samples the peak positions in the mid- 2θ region of $30\text{--}50^\circ$ ($2.7\text{--}1.8\text{ Å}$) differ from each other. The reflections in the mid- 2θ could be indexed to $h0l/OkI$ reflections and can be used as indicators to identify the specific stacking sequence of layers with respective to each other. This provides direct evidence that the two samples crystallize in two different polytypes [23]. Polytypism in the case of layered double hydroxides is extensively studied [24,25]. The nature of the cations within the layer and the interlayer anions dictate the stacking sequence of layers in layered double hydroxides [9,23]. To the best of our knowledge there are no reports on the polytypism in layered hydroxysalts. In order to differentiate the polytypes in layered hydroxysalts, DIFFaX code was used. It enables us to simulate the PXRD patterns of layered structure. In order to simulate the PXRD patterns we need to describe the crystal structure in terms of stacking individual layers on top of each other. There are no reports of the single crystal structure data of these compounds. In such instances, the atomic position coordinates were taken from $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ crystal structures, respectively and the z -coordinates were modified in order to maintain the M–O bond distance [26]. We have described the overall structure of the layered compound in terms of the packing of anions. We used the symbols A, B and C to represent hydro-

xyl ion positions and symbols a, b and c to represent cation positions. The metal hydroxide slab, $[\text{M}(\text{OH})_2]$ can be represented by the symbol AbC or more simply as AC. Pure 1H polytype comprises of a hexagonal stacking sequence of AC AC AC-layers. We follow the Bookin and Drits nomenclature to represent different type of stacking sequences [27]. The number '1' denotes the layered periodicity and 'H/R' stands for the hexagonal/rhombohedral stacking. Different type of polytypes was generated by using distinct stacking sequences as described in the literature [15]. Structures with three-layer periodicity having the rhombohedral symmetry can be generated by only two sequences:

- (i) AC CB BA AC– $3R_1$; (ii) AC BA CB AC– $3R_2$.

The $3R_1$ polytype generates only prismatic interlayer sites, while the $3R_2$ generates only octahedral interlayer sites. The only way to distinguish one polytype from the other is to examine the relative intensities and the peak positions of different $h0l/OkI$ reflections. Similar observations have been reported in case of layered double hydroxides [23]. Fig. 2 shows the simulated PXRD patterns of 1H, $2H_2$, $2H_3$, $3R_1$ and $3R_2$ polytypes for nickel hydroxynitrate. We have also simulated the PXRD patterns of 1H, $2H_2$, $2H_3$, $3R_1$ and $3R_2$ polytypes for cobalt hydroxynitrate. The peak positions in the DIFFaX simulated PXRD patterns of the 1H polytype matches well with the observed PXRD pattern of nickel hydroxynitrate and could be indexed to 101, 102 and 103 reflections in the mid- 2θ region (see Fig. 1a and b). The broadening of $h0l$ reflections in the nickel hydroxynitrate can arise due to the presence of structural disorder [28]. The peak positions in the simulated PXRD pattern for $3R_2$ polytype matches well with the observed PXRD pattern of cobalt hydroxynitrate. The reflections were indexed to 101, 104 and 107 planes (see Fig. 1c and d). The simulated powder X-ray diffraction patterns of 1H and $3R_2$ polytypic modifications show similar peak positions in the low angle while the differences arises for $h0l/OkI$ reflections. We have shown qualitatively that the peak positions and the relative intensities of $h0l/OkI$ reflections in the PXRD patterns of nickel hydroxynitrate and cobalt hydroxynitrate samples provides information about the nature of polytypes. The misfit in the relative intensities of the peaks between the observed and simulated PXRD patterns could be due to the exclusion of the interlayer species during the DIFFaX simulations.

In summary, polytype selectivity can be exercised by the choice of the metal ion and the bonding between the metal-anion. For the first time, we have classified polytypes in layered hydroxysalts using PXRD simulation studies and conclude that nickel

Fig. 2. DIFFaX simulated PXRD patterns of (a) 1H, (b) $2H_2$, (c) $3R_1$ and (d) $3R_2$ polytypes of nickel hydroxynitrate, respectively.

hydroxynitrate crystallizes in 1H polytype, while cobalt hydroxynitrate crystallizes in 3R₂ type of polytype, respectively.

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