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Thermal properties of sodium–light-lanthanoid double sulfate monohydrates

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Abstract

The thermal decomposition of sodium–light-lanthanoid double sulfate monohydrates up to 1600°C has been studied by TG, DTG, DTA, IR and X-ray diffraction methods. The information obtained by IR and X-ray techniques verified the crystal structure of the $NaLn(SO_4)_2 \cdot H_2O$-type compounds. TG analyses revealed that after dehydration the decomposition reaction proceeds with the formation of $NaLnOSO_4$, then Ln_2OSO_4, with the removal of Na_2O, followed by $Ln_2O_2SO_4$ and finally the oxide of the lanthanide is formed. It was found that the cerium double sulfate decomposes anomalously. In the dehydration stage, all the compounds exhibited a behavior that was different from that of the hydrated rare-earth sulfates.

INTRODUCTION

The thermochemistry of rare earth oxysalts has been reviewed over the years. Among many oxysalts, the rare earth sulfates are of special interest because their thermal degradation leads to the oxide by an oxysulfate intermediate [1, 2]. Both materials have interesting properties, being the starting substances in the preparation of superconductors, being suitable for catalytic uses [3–5], and exhibiting luminescence [6, 7]. It should be possible to improve these unique characteristics by building up the double salt structure with various cations.

A number of publications regarding the synthesis and characterization of lanthanoid double sulfate hydrates with monovalent cations have been reported. Preparative conditions alter the stoichiometry and the water content of these compounds. Salts of formula of $MLn(SO_4)_2 \cdot H_2O$ where M is sodium [8–11], potassium [12–14], rubidium [15], lithium [16], ammonium [17] and silver [18] have been described. However most of the thermal data have involved only the dehydration step. It is rather difficult to interpret the results and to identify the reaction intermediates over a wide

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temperature range because thermal analytical methods such as TG, DTA and DSC provide information of a dynamic nature.

The present work was initiated to examine the thermal decomposition of sodium–Ln (Ln is La, Ce, Nd, Sm) double sulfate monohydrates up to 1600°C. The changes in the infrared and X-ray diffraction patterns of the hydrates, the corresponding anhydrous salts and the final degradation products were determined. The results are assessed in order to ascertain a mechanism for the decomposition of the light-lanthanide–sodium double sulfates. The results are compared to data available for the simple sulfates.

EXPERIMENTAL

Preparation of the sodium–lanthanoid double sulfate monohydrates

The double sulfates (Ln is La, Nd, Sm), except the cerium salt, were prepared from the rare earth oxides (Merck). About 3 g of the corresponding oxide were dissolved in 1 M H_2SO_4 and diluted with distilled water to obtain a 0.05 M solution of the lanthanoid sulfate. Solid Na_2SO_4 (five-fold excess) was then added. The monohydrates, white for La, lilac for Nd, and creamy white for Sm, precipitated over several days after slow crystallization. The compounds were filtered through a medium porosity funnel, washed with cold water and dried below 100°C overnight.

The cerium compound was prepared in a similar manner except that 5 g of $Ce_2(SO_4)_3 \cdot 5H_2O$ (Merck) was first dissolved in 1 M H_2SO_4. For complete dissolution, 7 cm^3 of H_2O_2 was added and the solution was diluted to a concentration of 0.04 M of cerium sulfate. The resulting solution was mixed with an equimolar Na_2SO_4 solution, heated to 50–60°C for about an hour and left to crystallize. The white precipitates were filtered, washed with cold water and dried under an IR lamp.

The sodium–lanthanoid double sulfate monohydrates were identified by chemical composition analysis and by IR and X-ray diffraction techniques. Lanthanide and sodium ions were determined using a Shimadzu ICPS-1000 II sequential spectrophotometer. The water of crystallization was determined by thermogravimetry using a DuPont 951 TG connected to a DuPont 9900 thermal analyzer. The total sulfate content was obtained by subtracting the sum of the sodium, lanthanide and water contents from 100%.

The $Ln_2(SO_4)_3 \cdot nH_2O$ compounds were prepared by dissolving 1 g of the lanthanide oxide in 1 M H_2SO_4. The solutions were heated to 50°C and concentrated. The resulting crystals were used in the thermal studies in order to obtain data that could be compared with those of the double sulfates. TG analyses showed that the compounds were $La_2(SO_4)_3 \cdot 9H_2O$, $Ce_2(SO_4)_3 \cdot 5H_2O$, $Nd_2(SO_4) \cdot 8H_2O$ and $Sm_2(SO_4)_3 \cdot 8H_2O$.

Thermal analysis

The decomposition of the sodium–lanthanoid double sulfate monohydrates was studied by dynamic thermogravimetry and differential analysis techniques. The TG measurements were carried out on a Setaram TGA 92 instrument up to 1600°C under the following conditions: sample weight, approx. 50 mg (particle size 150 mesh); dynamic argon atmosphere, flow rate 26.7 $cm^3 min^{-1}$; Pt/Pt–Rh 10% thermocouples; platinum crucibles (130 μl); heating program, 25 to 1600°C at 2°C min^{-1}, isothermal at 1600°C for 5 min, 1600 to 25°C at 30°C min^{-1}.

The DTA curves were obtained using a Netzsch 404 instrument up to 1400°C under the following conditions: sample weight, approx. 50 mg (particle size 150 mesh); dynamic nitrogen atmosphere; ceramic crucibles; Pt/Pt–Rh 10% thermocouples; heating rate, 10°C min^{-1}.

FTIR and X-ray diffraction measurements

FTIR data were recorded on a Shimadzu FTIR 8101 spectrometer at a resolution of 4 cm^{-1} employing the KBr disk method. X-ray diffraction patterns were obtained in a Phillips PW 1140/00 Dy 687 diffractometer using Cu Kα (λ = 1.542 Å) radiation with a Ni filter.

RESULTS

Hydrates

The chemical compositions of the sodium–lanthanoid double sulfate monohydrates are given in Table 1. The empirical formula $NaLn(SO_4)_2 \cdot H_2O$ was established by elemental analyses.

The FTIR spectra of the compounds yielded doublets in the region of 3600–3500 cm^{-1} corresponding to the O–H stretching mode as shown in Fig. 1. In the 1620–1610 cm^{-1} region, the O–H bending vibrations ap-

TABLE 1

Results of elemental and thermal analysis for $NaLn(SO_4)_2 \cdot H_2O$

Ln	Na/mol		Ln/mol		SO_4^{2-}/mol		H_2O/mol	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
La	0.269	0.324	0.268	0.298	0.535	0.483	0.269	0.264
Ce	0.268	0.296	0.270	0.275	0.536	0.522	0.268	0.261
Nd	0.265	0.296	0.275	0.298	0.521	0.487	0.265	0.279
Sm	0.261	0.324	0.282	0.327	0.530	0.441	0.261	0.257

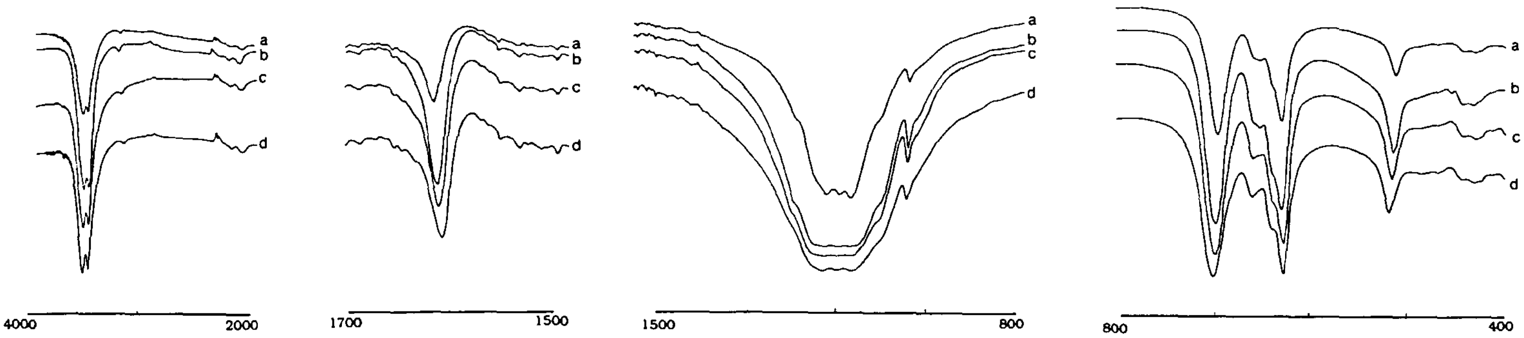


Fig. 1. FTIR spectra of: curve a, $NaLa(SO_4)_2 \cdot H_2O$; curve b, $NaCe(SO_4)_2 \cdot H_2O$; curve c, $NaNd(SO_4)_2 \cdot H_2O$; and curve d, $NaSm(SO_4)_2 \cdot H_2O$.

peared as singlets. The doublets shifted to lower frequencies by a few wavenumbers as the atomic mass number of the lanthanide metal increased. Of the four sulfate fundamentals, the infrared-active ν_3 and ν_4 modes were observed at about 1100 and 625 cm^{-1}, respectively. The ν_3 vibration appeared as a strong, broad band with shoulders on either side and was split into three, while ν_4 was split into more bands. The infrared-inactive ν_1 (1010–1005 cm^{-1}) and ν_2 (505–420 cm^{-1}) modes also became noticeable, at medium intensity. The ν_2 vibration showed a rather complex pattern by mixing with the librational modes of the hydrate water, undergoing a marked change upon dehydration. All the bands moved slightly but progressively to higher frequencies as the rare earth metal was replaced by a heavier one. A small peak at 2350 cm^{-1} corresponding to the absorbed carbon dioxide was observed in the spectra of the monohydrates.

The X-ray powder diffraction data for the hydrated double salts are summarized in Table 2. The observed *d*-spacings and intensities are listed with the previously reported experimental and calculated values for the isostructural compounds. The data indicate that the materials obtained are isomorphous.

TABLE 2

X-ray powder data for $NaLn(SO_4)_2 \cdot H_2O$ (Ln is La, Ce, Nd, Sm)

$d_{obs}/Å$ [a]				I_{obs} [a]	$d_{obs}/Å$ [b]	I_{obs} [b]	$d_{calc}/Å$ [b]
La	Ce	Nd	Sm				
6.062	6.062	5.980	5.980	vs	5.426	vs	5.437
5.500	5.500	5.273	5.273	vs	5.426	vs	5.437
4.329	4.329	4.350	4.350	w	4.400	m	4.383
4.300	4.300	4.267	4.267	vw	4.270	w	4.277
3.504	3.504	3.463	3.463	s	3.461	s	3.465
3.386	3.386	3.348	3.348	vw	3.346	w	3.346
3.046	3.025	2.999	2.999	vs	3.005	vs	3.001
2.957	2.957	2.919	2.919	vw	2.913	w	2.922
2.85	2.846	2.820	2.820	vs	2.829	vs	2.829
2.720	2.720	2.680	2.700	vw	2.700	w	2.693
2.486	2.479	2.453	2.447	vw	2.457	m	2.457
2.378	2.372	2.348	2.348	w	2.356	m	2.356
2.263	2.257	2.231	2.225	vw	2.274	w	2.269
2.215	2.210	2.189	2.189	vw	2.235	w	2.234
2.170	2.159	2.135	2.130	w	2.196	w	2.192

Key: m means medium; s means strong; v means very; w means weak. [a] Present work. [b] For isostructural $NaPu(SO_4)_2 \cdot H_2O$ [11] and $NaCe(SO_4)_2 \cdot H_2O$ [19].

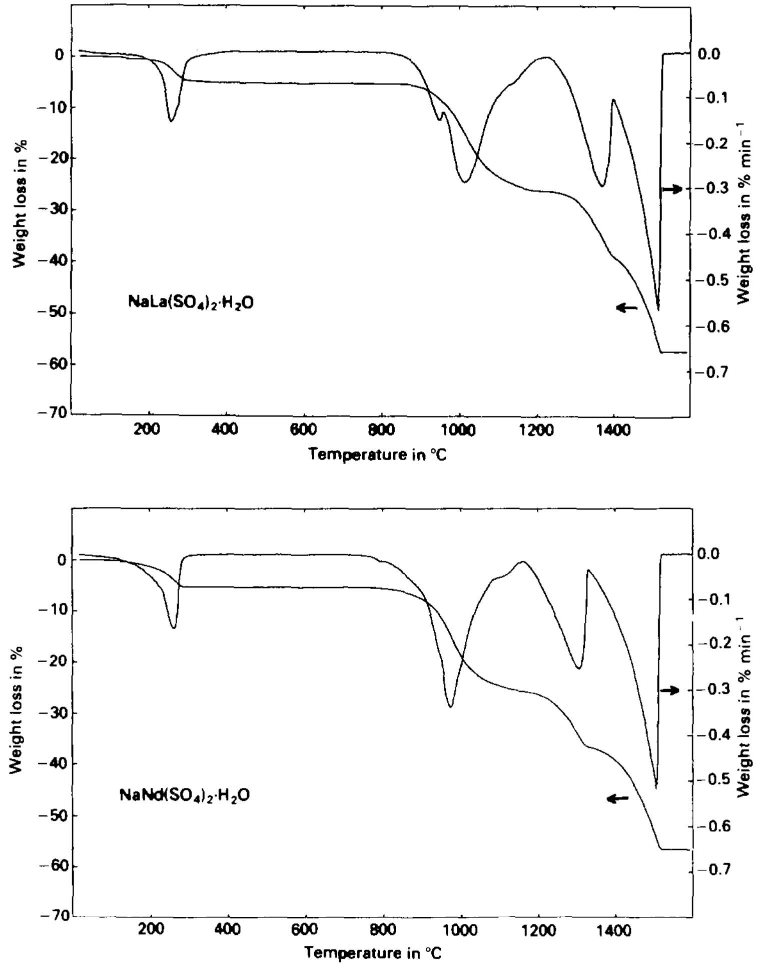
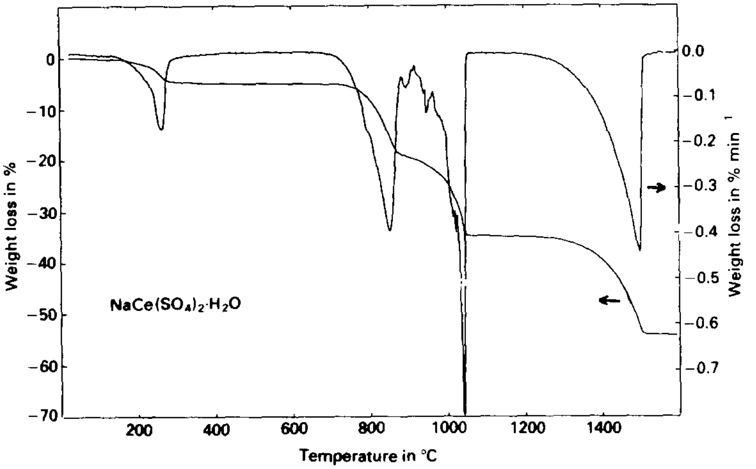


Fig. 2. TG and DTG curves of sodium–lanthanoid double sulfate monohydrates.

Dehydration

The thermal analysis curves of the double salts are shown in Fig. 2. For the lanthanum compound, the presence of a shoulder on the DTG peak suggests that fractional dehydration occurs with the removal of one mole of water, while for the other compounds dehydration proceeds in one step. The dehydration and decomposition temperatures for both $Ln_2(SO_4)_3 \cdot nH_2O$ and $NaLn(SO_4)_2 \cdot H_2O$ are given in Table 3. Dehydration onset temperatures were not taken into account because of the presence of a minor amount of adsorbed surface water on some samples. It was found that the temperature for the release of water decreases with decreasing ionic radius of Ln^{3+} for the double sulfates. This is in contrast to the behavior of $Ln_2(SO_4)_3 \cdot nH_2O$, as noted before [21] and as observed in this work.



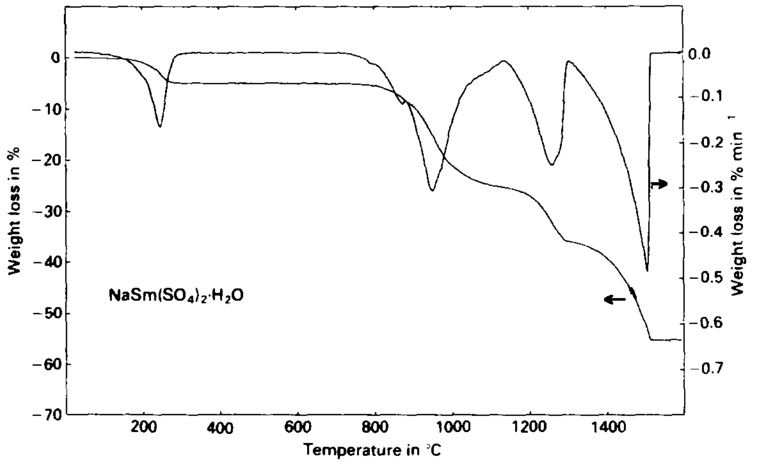


Fig. 2 (continued).

DTA yielded a broad featureless band for the dehydration of the lanthanum double sulfate while the other curves showed more clear endotherms corresponding to the dehydration step. Exotherms were also observed for the Nd and Sm double salts at around 520, 480 and 450°C, respectively. Because they did not correspond to any weight change, these must be due to phase transitions to the crystalline state. The X-ray diffraction data of the samples heated up to 600–700°C, just below the next decomposition temperature, showed some variations. The Nd and Sm double salts gave quite similar patterns, while the cerium compound obtained at 350°C resembled that of La at 600°C.

On heating to 600°C, the O–H bending vibrations and the water librational mode at 500 cm^{-1} disappeared, and the O–H stretching vibrations decreased greatly in intensity. No significant change was observed in the sulfate vibrations after dehydration except that the ν_2 vibrations became

TABLE 3

Temperatures corresponding to the dehydration and decomposition of $Ln_2(SO_4)_3 \cdot nH_2O$ and $NaLn(SO_4)_2 \cdot H_2O$ (Ln is La, Ce, Nd, Sm)

Compound	Dehyd. peak temp./°C (DTG)	Dehyd. offset temp./°C (TG)	Decomp. onset temp./°C (TG)	Eff. ionic radius of Ln^{3+}/pm [a]
$La_2(SO_4)_3 \cdot 9H_2O$	–	288	800	135.6
$NaLa(SO_4)_2 \cdot H_2O$	259 + 279	297	856	135.6
$Ce_2(SO_4)_3 \cdot 5H_2O$	–	391	694	133.6
$NaCe(SO_4)_2 \cdot H_2O$	271	285	712	133.6
$Nd_2(SO_4)_3 \cdot 8H_2O$	–	365	759	130.3
$NaNd(SO_4)_2 \cdot H_2O$	265	276	800	130.3
$Sm_2(SO_4)_3 \cdot 8H_2O$	–	647	688	127.2
$NaSm(SO_4)_2 \cdot H_2O$	250	265	762	127.2

[a] For nine coordination [20].

more clear and intensified. Continued heating of the materials resulted in the complete loss of bands assignable to water vibrations.

Decomposition of the anhydrous salts

After dehydration, a long plateau is observed on the DTA curve indicating the stability of the anhydrous double sulfates. The stability range extends to about 800°C (lower for Ce). The observed and calculated weight losses, based on the stepwise decomposition reactions and the temperature ranges, are summarized in Table 4. The thermal properties of the La, Nd and Sm compounds are similar, although the decomposition onsets shift to lower temperatures on moving from La to Sm. Cerium displays a different thermal behavior.

The anhydrous sulfates decompose via several reactions accompanied by a release of mainly SO_2 and O_2. The TGA data indicate that the decompositions occur in three steps: firstly, two molecular equivalents of SO_3 are expelled; then at a higher temperature, Na_2O is removed, yielding the oxysulfates; finally the oxysulfates decompose to the oxides. The DTA studies also indicate this decomposition pattern, giving three endothermic peaks. The third, broad endotherm was assigned to the formation of the oxide. No reversible process was recorded.

Calculations based on the mass losses observed in the curves were in good agreement with the information obtained from the IR spectra. On heating, a regular decrease in both the intensities and the splittings of the ν_3 and ν_4 modes was observed, while ν_1 and ν_2 disappeared. The final products indicate no sulfate bands and their spectra corresponded to the lanthanide oxides except for lanthanum oxide which also showed hydroxide

TABLE 4

Decomposition stages and related data for the compounds $NaLn(SO_4)_2 \cdot H_2O$

Decomposition state	Temp. range DTG/°C	Weight loss/%	
		Calc.	Obs.
$2NaLa(SO_4)_2 \cdot H_2O \rightarrow 2NaLa(SO_4)_2 + 2H_2O$	···–259–297	4.8	5.0
$2NaLa(SO_4)_2 \rightarrow 2NaLaOSO_4 + 2SO_2 + O_2$	888–1014–1235	22.6	21.6
$2NaLaOSO_4 \rightarrow La_2O(SO_4)_2 + Na_2O$	1235–1370–1403	11.3	11.1
$[La_2O(SO_4)_2 \rightarrow La_2O_2SO_4 + SO_2 + 0.5O_2]$			
$La_2O_2SO_4 \rightarrow La_2O_3 + SO_2 + 0.5O_2$	1403–1521–1529	19.7	19.1
Overall reaction			
$2NaLa(SO_4)_2 \rightarrow La_2O_3 + Na_2O + 2H_2O + 4SO_2 + 2O_2$		56.2	56.8
$2NaNd(SO_4)_2 \cdot H_2O \rightarrow 2NaNd(SO_4)_2 + 2H_2O$	···–265–276	4.8	5.0
$2NaNd(SO_4)_2 \rightarrow 2NaNdOSO_4 + 2SO_2 + O_2$	876–973–1165	22.3	20.0
$2NaNdOSO_4 \rightarrow Nd_2O(SO_4)_2 + Na_2O$	1165–1306–1132	11.1	11.1
$[Nd_2O(SO_4)_2 \rightarrow Nd_2O_2SO_4 + SO_2 + 0.5O_2]$			
$Nd_2O_2SO_4 \rightarrow Nd_2O_3 + SO_2 + 0.5O_2$	1132–1509–1515	19.2	20.3
Overall reaction			
$2NaNd(SO_4)_2 \rightarrow Nd_2O_3 + Na_2O + 2H_2O + 4SO_2 + 2O_2$		55.4	56.4
$2NaSm(SO_4)_2 \cdot H_2O \rightarrow 2NaSm(SO_4)_2 + 2H_2O$	···–250–285	4.7	4.8
$2NaSm(SO_4)_2 \rightarrow 2NaSmOSO_4 + 2SO_2 + O_2$	800–953–1138	21.9	20.9
$2NaSmOSO_4 \rightarrow Sm_2O(SO_4)_2 + Na_2O$	1138–1259–1309	10.9	10.2
$[Sm_2O(SO_4)_2 \rightarrow Sm_2O_2SO_4 + SO_2 + 0.5O_2]$			
$Sm_2O_2SO_4 \rightarrow Sm_2O_3 + SO_2 + 0.5O_2$	1309–1506–1521	18.7	19.3
Overall reaction			
$2NaSm(SO_4)_2 \rightarrow Sm_2O_3 + Na_2O + 2H_2O + 4SO_2 + 2O_2$		54.5	55.0
$2NaCe(SO_4)_2 \cdot H_2O \rightarrow 2NaCe(SO_4)_2 + 2H_2O$	···–271–285	4.8	4.8
$2NaCe(SO_4)_2 \rightarrow 2NaCeOSO_4 + 2SO_2 + O_2$			
$2NaCeOSO_4 \rightarrow Ce_2O(SO_4)_2 + Na_2O$	750–···–1062		29.9
$Ce_2O(SO_4)_2 \rightarrow Ce_2O_3SO_4 + SO_2$			
$Ce_2O_3SO_4 \rightarrow CeO_2 + SO_2 + 0.5O_2$	1212–1500–1512	18.9	18.9
Overall reaction			
$2NaCe(SO_4)_2 \cdot H_2O \rightarrow 2CeO_2 + Na_2O + H_2O + 4SO_2 + 1.5O_2$		53.9	53.6

(3625 cm^{-1}, sh) and carbonate (1500, 1350 cm^{-1}) peaks. X-ray data show that the final products were $La(OH)_3$, CeO_2, Nd_2O_3 and Sm_2O_3 (Table 5). The TG curves revealed a total weight loss of 56.8%, 53.6%, 56.4% and 55.0% respectively for La, Ce, Nd and Sm double sulfate monohydrates. These values agree well with the theoretical weight losses calculated from the assumed decomposition scheme.

TABLE 5

d Spacings and relative intensities of the final decomposition products of $NaLn(SO_4)_2 \cdot H_2O$ (Ln is La, Ce, Nd, Sm)

La	Ce	Nd	Sm
5.63(vs)	3.10(vs)	3.32(w)	3.18(vw)
3.26(vs)	2.69(m)	3.00(w)	3.00(vw)
3.16(s)	1.90(s)	2.90(vs)	2.97(vs)
2.82(vw)	1.62(s)	2.23(w)	2.90(vw)
2.49(vw)	1.56(vw)	1.92(w)	2.84(vw)
2.27(m)		1.71(w)	2.78(vw)
2.13(vw)		1.66(vw)	2.20(vw)
1.92(vw)		1.61(w)	2.15(vw)
1.88(m)		1.69(w)	1.93(vw)
1.86(s)		1.28(vw)	1.76(vw)
1.66(vw)		1.23(vw)	1.68(vw)
1.63(vw)		1.06(vw)	
1.59(vw)			
1.57(vw)			

The simple sulfates of La, Ce, Nd and Sm, in the form $Ln_2(SO_4)_3 \cdot nH_2O$, decomposed following almost the same mechanism as proposed by Wendlandt [1, 21], but the reaction temperatures observed in this work were different. Because of variations in the heating rates and the purity of the materials, these deviations are to be expected.

DISCUSSION

In addition to the elemental analysis results, the IR and X-ray data of the $NaLn(SO_4)_2 \cdot H_2O$ compounds verified the composition and structure of these salts. All the compounds reported here have the $NaCe(SO_4)_2 \cdot H_2O$-type structure in which the lanthanoid ion is coordinated by nine oxygen atoms; eight of these are sulfate oxygens and the ninth is the water oxygen [19]. Four oxygen atoms belonging to sulfate groups and the water form a puckered five-membered ring. The interaction of water with two nearest and two next-nearest oxygen neighbors results in splitting of the O–H stretching frequencies into a doublet (Fig. 1). Sodium ions are surrounded by eight oxygen atoms belonging to sulfate groups, with six long and two short bonds. There seems to be no short-range interaction between the water molecule and the alkali metal ion, nor any effective hydrogen bonding. The high coordination number of the Ln^{3+} ions and the absence of a broad band in the O–H stretching range indicate that water in the lanthanide sulfate is coordinately bound. The high temperature of dehydration confirms the strong bonding of water to the rare earth ion.

Trivalent Ln ions form a series of compounds with properties which vary regularly, reflecting the decreasing ionic radii of the cations along the series. One would expect an increase in the dehydration temperatures owing to the increasing cation solvation energy, as observed for the hydrated sulfates of lanthanides [21, present work] and also for the hydrated sodium lanthanide double sulfates [9]. However, the reverse behavior was noted (Table 2). The decrease in dehydration temperatures from La to Sm was also established by a second set of experiments carried out on a DuPont 951 TG. For the La, Nd and Sm sulfates, we observed exotherms in the DTA curves due to crystallization at 520, 480 and 450°C respectively. This is again unexpected for dehydration because the crystallization of anhydrous rare earth sulfates is known to take place at higher temperatures from La to Gd [22]. We were unable to discern an exotherm for the Ce compound. It appears that the presence of sodium ions particularly influences the initial stages of the general decomposition scheme by lowering the activation energies of dehydration and crystallization from lanthanum to samarium.

Lindgren [19] reported that the sulfate groups act as unidentate ligands in the equatorial directions and bidentate in axial directions. This change in symmetry and lattice effects splits the degenerate vibrations and activates the infrared-inactive vibrations of the sulfate group. On coordination, all of the fundamentals are shifted according to their modes of vibration. As the metal–ligand bond becomes stronger, their shifts to lower or higher frequencies increase [23]. We observed that the bands shifted to progressively higher frequencies by a few wavenumbers following the polarizing power of the cation. Hester and Krishnan [24] observed a similar trend in the vibrational spectra of some molten sulfates. The strengthening of the Ln–O coordinate bonds in the series of lanthanides with decreasing ionic radius [25], creates a more pronounced distortion of the sulfato groups, hence lowering the decomposition onset temperatures of the anhydrous salts. The decomposition temperature of the Ce complex was not included because a different chemical reaction occurs on heating. When heated to high temperatures, the anhydrous double sulfates decompose through the initial loss of SO_2 and O_2. The decomposition onset temperatures are higher than the simple sulfates although they follow the same trend from La to Sm. If the variations in the dehydration temperatures of these two types of salts are considered, the role of the Na^+ ions in stabilizing the anhydrous sulfates is noteworthy.

The first step of the decomposition results in the formation of $NaLnOSO_4$. We did not observe the dissociation of the double sulfate into its components before the decomposition, as suggested by Zaitseva et al. [9]. In the second step, $NaLnOSO_4$ decomposes to $Ln_2O(SO_4)_2$ with the removal of Na_2O. The dissociation pressure of sodium sulfate is notably lower than that of lanthanide sulfate, as is also apparent from the bond strengths of Na–O (≈ 250 kJ mol^{-1}) and Ln–O (> 700 kJ mol^{-1}). Thus, degradation of the sulfato–sodium groups by the evolution of sulfur oxides yields Na_2O, which sublimes to yield $Ln_2O(SO_4)_2$ at temperatures higher than 1000°C. Further heating of $Ln_2O(SO_4)_2$ yields $Ln_2O_2SO_4$ which decomposes to the oxide. IR data show that oxide formation is completed in the third step. The complicated nature of the TG curves suggests that the decomposition reaction is accompanied by various overlapping processes. In the final step, the weight loss is significantly lower than expected for the dioxysulfate formation. This discrepancy may be attributed to the simultaneous decomposition of the dioxysulfate to the oxide before all the dioxysulfate has been formed via oxydisulfate. We did not observe a stable dioxysulfate phase, as was observed for $La_2O_2SO_4$ [6]. None of the intermediates could be isolated in pure form due to the overlap of the processes.

The decomposition of the Ce double salt, as reflected by the mass losses observed over the temperature range 700–1600°C, is considered to be a redox reaction written overall as

$$2NaCe(SO_4)_2 \rightarrow 2CeO_2 + Na_2O + 4SO_2 + 1.5O_2$$

The variation in the valence of cerium with increasing temperature has been investigated before [4]. It has been found that Ce(IV) predominates above $\approx$720°C. The overlapping thermal steps confirm that oxidation occurs at the same time as decomposition. This might be the reason for the absence of an exotherm corresponding to the oxidation of Ce in the DTA. We hypothesize the formation of a trioxysulfate intermediate. Although this was never observed before, the mass loss agrees well with the observed data.

The thermal decomposition of the sodium lanthanoid double sulfates yields the sesquioxides, while cerium double sulfate results in CeO_2. X-ray powder patterns of the final degradation products indicate a single crystalline phase. Together with the IR data, X-ray diffraction analysis suggests formation of lanthanum hydroxide with some carbonate formation. The hydration of oxides to hydroxides and absorption of CO_2 to form basic carbonates are characteristic properties of rare earth oxides [26]. The tendency to absorb moisture and carbon dioxide decreases gradually with increasing atomic number. The most basic lanthanum oxide rapidly absorbs moist air and, in time, the composition $La(OH)_3$ is approached.

CONCLUSIONS

Sodium–lanthanoid double sulfate monohydrates decompose thermally before dissociation into their component salts. In the first step of decomposition, a sodium–lanthanoid oxysulfate intermediate is formed which subsequently undergoes decomposition to Na_2O and lanthanide dioxysulfate. Na_2O sublimes above 1000°C and then the decomposition follows a similar mechanism to those of the simple lanthanoid sulfates. The cerium double salt exhibits a different mechanism, resulting in the formation of CeO_2.

The general decomposition scheme can be summarized as

$$NaLn(SO_4)_2 \cdot H_2O \rightarrow NaLn(SO_4)_2 + H_2O$$

$$2NaLn(SO_4)_2 \rightarrow 2NaLnOSO_4 + 2SO_2 + O_2$$

$$2NaLnOSO_4 \rightarrow Na_2O + Ln_2O(SO_4)_2$$

$$Ln_2O(SO_4)_2 \rightarrow Ln_2O_2SO_4 + SO_2 + 0.5O_2$$

$$Ln_2O_2SO_4 \rightarrow Ln_2O_3 + SO_2 + 0.5O_2$$

The isolation and characterization of the intermediates are difficult because of the overlapping thermal steps.

The decomposition onset temperatures decrease with decreasing ionic radius of the Ln^{3+} ion. The dehydration and crystallization temperatures also decrease on moving from La to Sm. The double salts start to decompose at higher temperatures than the simple salts which also indicates the stability of the anhydrous phase in the presence of sodium ions.

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REFERENCES

1 M.W. Nathans and W.W. Wendlandt, J. Inorg. Nucl. Chem., 24 (1962) 869.
2 A. Saito, Thermochim. Acta, 24 (1988) 217.
3 M.P. Rosynek, Catal. Rev., 16 (1977) 111.
4 E.J. Peterson, E.M. Foltyn and E.I. Onstott, J. Am. Chem. Soc., 105 (1983) 7572.
5 M. Leskelä, J.E.X. de Matos and L. Niinistö, Inorg. Chim. Acta, 139 (1987) 121.
6 J.W. Haynes and J.J. Brown, J. Electrochem. Soc., 115 (1968) 1060.
7 J.F. Lynch, C.J. Sachcs and H.G. Brittain, Thermochim. Acta, 109 (1987) 343.
8 L.L. Zaitseva, M.I. Konarev, A.A. Kruglov and N.T. Chebotarev, Russ. J. Inorg. Chem., 9 (1964) 1380.
9 L.L. Zaitseva, M.I. Konarev, M.A. Kruglov, E.P. Cherstvenkova and V.I. Yaroshinskii, Russ. J. Inorg. Chem., 10 (1965) 783.
10 A.P. Belouseva, I.V. Shakhno and V.E. Plyuschev, Russ. J. Inorg. Chem., 13 (1968) 1037.
11 P.N. Iyer and P.R. Natarajan, J. Less-Common Met., 146 (1989) 161.
12 K.I. Petrov, G.N. Voronskaya, L.D. Ishakova and V.E. Plyuschev, Russ. J. Inorg. Chem., 16 (1971) 675.
13 V.S. Ilyashenko, A.N. Barabash and L.L. Zaitseva, Russ. J. Inorg. Chem., 18 (1973) 1510.
14 A.I. Barabash, L.L. Zaitseva and V.S. Ilyashenko, Russ. J. Inorg. Chem., 17 (1972) 2001.
15 N.L. Sarukhanyan, L.D. Iskhakova, E.P. Monochenets and V.K. Trunov, Zh. Neorg. Khim., 27 (1982) 1963.
16 L.D. Iskhakova, C.A. Bondar and V.K. Trunov, Zh. Neorg. Khim., 32 (1987) 328.
17 P.N. Iyer and P.R. Natarajan, J. Less-Common Met., 159 (1990) 1.

18 V. Jordanovska and J. Shiftar, Thermochim. Acta, 209 (1992) 259.
19 O. Lindgren, Acta Chem. Scand., 7 (1977) A 31.
20 R.D. Shannon, Acta Crystallogr. Sect. A, 32 (1969) 751.
21 W. Wendlandt, J. Inorg. Nucl. Chem., 7 (1958) 51.
22 A. Saito, Thermochim. Acta, 124 (1988) 217.
23 K. Nakamoto, J. Fujida, S. Tanaka and M. Kobayashi, J. Am. Chem. Soc., 79 (1957) 4904.
24 R.E. Hester and K. Krishnan, J. Chem. Phys., 49 (1968) 4356.
25 K. Negase, Bull. Chem. Soc. Jpn., 45 (1972) 2166.
26 T. Sato, Thermochim. Acta, 148 (1989) 249.