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Synthesis, Characterization, and Thermal Decomposition of Double Rare Earth Monomethylammonium Selenates

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Summary. Double rare earth monomethylammonium selenates of the general formula $CH_3NH_3\mathit{Ln}(SeO_4)_2\cdot 5H_2O$ (Ln = Sm, Eu, Gd, Tb, Ho, Y) were synthesized and characterized using X-ray powder diffraction and infrared spectroscopy. The thermal decomposition of the compounds were investigated using TG, DTG, and DTA techniques.

Keywords. Rare earths; Double rare earth monomethylammonium selenates; Infrared spectra; Thermal decomposition; X-Ray powder diffraction.

Introduction

There are many reports in the literature dealing with spectroscopic and thermal studies of double sulfates and selenates of tervalent rare earths with monovalent cations of the general empirical formula $M\mathit{Ln}(XO_4)_2\cdot nH_2O$ (M = alkali metal, Tl^+, or NH_4^+; X = S or Se). Investigations on the double sulfates of rare earths with mono-, di-, tri-, and tetramethylammonium ions have also been carried out extensively in the last two decades [1–11]. Research on the corresponding double alkylammonium selenates has, however, been restricted to those of sodium [12], magnesium, nickel [13], and some trivalent metal ions like aluminum, gallium, and chromium [14–19]. Since there are no reports on the double selenates of rare earths with alkylammonium ions, it was thought worthwhile to synthesize these compounds in our laboratory and study their physical and chemical properties.

Results and Discussion

The synthesis of double selenates of rare earths containing the methylammonium ion were attempted with molar ratios of rare earth selenate to monomethylammonium selenate (*MMAS*) from 1:1 to 1:5. The compounds precipitated at a molar ratio of 1:1 were found to be single rare earth selenate octahydrates. The infrared spectra of these compounds showed no bands characteristic of the monomethylammonium ion. The results of chemical analyses of the compounds obtained with

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Table 1. Results of chemical analysis of the double rare earth monomethylammonium selenates of the general formula $CH_3NH_3Ln(SeO_4)_2{\cdot}5H_2O$

Ln	% *Ln*		% SeO_4		% N		% H_2O	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
Sm	26.93	26.19	51.20	51.41	2.51	2.37	16.13	16.14
Eu	27.14	26.75	51.05	51.36	2.50	2.75	16.08	16.39
Gd	27.82	27.10	50.58	51.19	2.48	2.41	15.93	15.90
Tb	28.03	27.18	50.43	50.26	2.47	2.44	15.88	16.18
Ho	28.78	27.73	49.89	49.63	2.44	2.38	15.72	16.13
Y	17.89	17.47	57.53	58.36	2.82	2.68	18.12	17.58

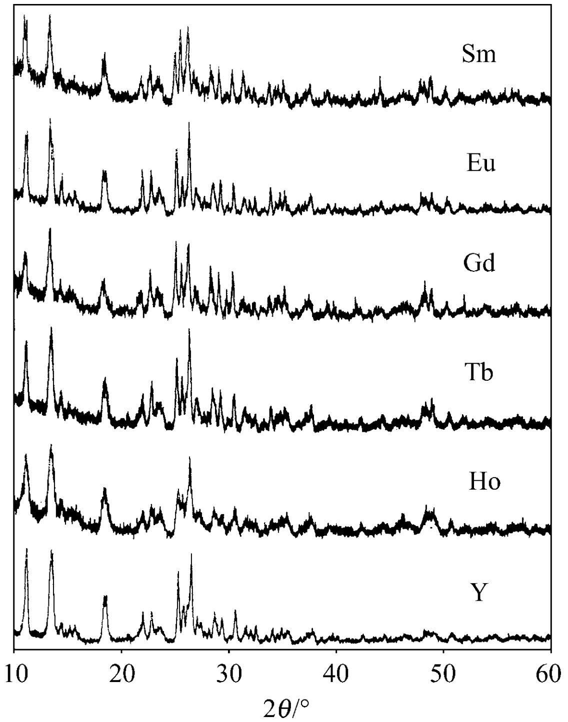

Fig. 1. X-Ray powder diffractograms of $CH_3NH_3Ln(SeO_4)_2{\cdot}5H_2O$

molar ratios from 1:2 to 1:5 given in Table 1 suggest that they have the general formula $CH_3NH_3Ln(SeO_4)_2{\cdot}5H_2O$, irrespective of the molar ratio applied. The X-ray powder diffractograms (Fig. 1) of all compounds were found to be similar, suggesting that they are isomorphous.

The infrared spectroscopic data in the range 4000–400 cm^{-1} are given in Table 2 (for the spectrum of the samarium salt, see Fig. 4a). The assignments of the bands were performed by comparison with literature data [12, 18, 20]. The spectra of the hydrated salts show a very broad band centered around 3250 cm^{-1} with weak shoulders on the lower-frequency side. The antisymmetric and symmetric stretching

Table 2. IR data of $CH_3NH_3\mathit{Ln}(SeO_4)_2{\cdot}5H_2O$ (cm^{-1})

Sm	Eu	Gd	Tb	Ho	Y	Assignments
3283br	3262br	3240br	3250br	3252br	3244br	$\nu(H_2O) + \nu(NH_3)$
2961sh	2974sh	2968sh	2854sh	2972sh	2876sh	$\nu(CH_3)$
2581sh	2561sh	2561sh	2559sh	2559sh	2559sh	
1651s	1667s	1662s	1667s	1657s	1664s	$\delta(H_2O)$
1558sh	1566sh			1558sh	1564sh	NH_3 antisymm. bending
1512s	1512s	1514s	1512s	1514s	1514s	NH_3 symm. bending
1462s	1464s	1466s	1466s	1466s	1466s	CH_3 antisymm. bending
1435m	1436vw	1435w	1437w	1435w	1435w	CH_3 symm. bending
1271w	1271w	1271w	1271w	1271w	1271w	NH_3^+ rocking
1018m		1018m	1018m		1018m	ν(C–N)
937sh		925sh	937sh	937sh		$\nu_3(SeO_4)$
883s	883s	887s	887s	881s	887s	
856sh	858sh	856sh	856sh	855sh	854sh	
	840sh				843sh	
833sh	831sh	835sh	837sh	837sh		$\nu_1(SeO_4)$
707br	709br	717br	723br	713br	713br	*Ln*–OH rocking
598br	592br	601br	588br	605br	609br	*Ln*–OH wagging

vibrations of NH_3^+ and those of OH^- overlap, making the assignment difficult. The shoulders probably owe their origin to the stretching modes of the CH_3 group. The band with a minimum at around ~1650 cm^{-1} is attributable to H–O–H bending vibrations; it appears as broad band with a shoulder at *ca.* 1600 cm^{-1} which can be assigned to the antisymmetric NH_3^+ deformation vibration. The band at 1514 cm^{-1} can be ascribed to the symmetric NH_3^+ deformation vibration, and that at 1464 cm^{-1} to the antisymmetric CH_3 deformation vibration. A weak band at ~1270 cm^{-1} is due to the NH_3^+ rocking mode. The internal vibrations of the selenate ions appear in the region below 1000 cm^{-1}. The bands at 934, 880, and 855 cm^{-1} are characteristic of ν_3 antisymmetric stretching vibrations, and the band at 840 cm^{-1} originates from ν_1 symmetric stretching vibrations. The weak and broad bands with minima at 710 and 600 cm^{-1} are attributable to the rocking and wagging modes of the coordinated water, respectively.

The thermogravimetric (TG) and differential thermal analysis (DTA) curves of europium monomethylammonium selenate (selected as a representative) recorded in the temperature range from 20 to 1000°C are shown in Figs. 2 and 3; the TG data of all compounds are collected in Table 3. The TG curves of all compounds are found to be similar, exhibiting three major weight losses. The first stage corresponds to dehydration, which commences above 90°C and is complete at about 200°C with the formation of anhydrous rare earth monomethylammonium selenate. The corresponding DTG curves exhibit a single peak in the case of samarium, europium, gadolinium, and yttrium compounds. The DTA curves of these compounds, however, contain a sharp endothermic peak followed by a shoulder, suggesting that the dehydration probably occurs in two overlapping stages which are not resolved. The DTG as well as the DTA curves of the terbium and holmium compounds exhibit two peaks, clearly indicating a two-step process.

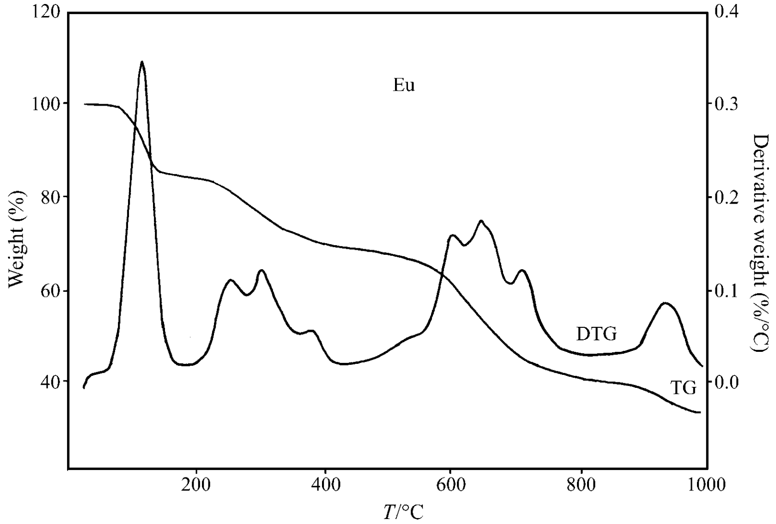

Fig. 2. TG and DTG curves of $CH_3NH_3Eu(SeO_4)_2{\cdot}5H_2O$ (sample weight: 15.271 mg)

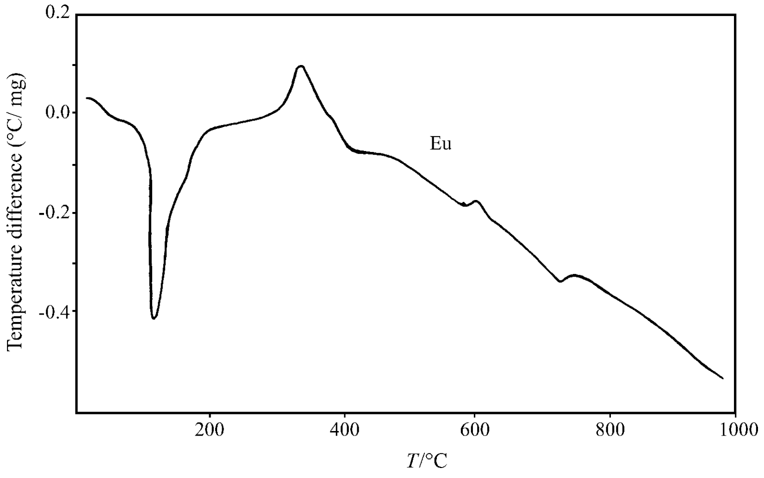

Fig. 3. DTA curve of $CH_3NH_3Eu(SeO_4)_2{\cdot}5H_2O$ (sample weight: 9.800 mg)

The anhydrous rare earth monomethylammonium selenates are stable over a very narrow temperature interval and begin to decompose just above 220°C. The TG curves show a rapid weight loss up to *ca.* 350°C, followed by a very gradual one up to ~500°C. The DTG curves show two to three peaks in the temperature range of 250 to 400°C, the first of which probably corresponds to the loss of methylamine. The DTA curves depict a broad exothermic peak corresponding to this stage. The weights of the residues remaining at *ca.* 350°C correspond to intermediates of the composition $Ln_2Se_4O_{11}$, whereas those at ~500°C suggest the formation of $Ln_2Se_{3.5}O_{10}$. It can thus be concluded that both selenites coexist in the temperature range from 350 to 500°C. The third major weight loss begins above ~500°C in each case. There is a change in the slope of the TG curve at

Table 3. Results of thermal analysis of $CH_3NH_3Ln(SeO_4)_2 \cdot 5H_2O$

Ln	TG Temperature (°C)	Composition of product	% Weight loss obsd.	% Weight loss calcd.
Sm	200	$CH_3NH_3Sm(SeO_4)_2$	16.12	16.13
	360	$Sm_2Se_4O_{11}$	30.32	29.04
	500	$Sm_2Se_{3.5}O_{10}$	34.43	34.01
	800	Sm_2SeO_5	60.09	59.16
Eu	200	$CH_3NH_3Eu(SeO_4)_2$	16.04	16.08
	360	$Eu_2Se_4O_{11}$	29.03	29.04
	550	$Eu_2Se_{3.5}O_{10}$	33.55	33.91
	800	Eu_2SeO_5	59.68	58.67
	1000	Eu_2O_3	67.55	68.58
Gd	200	$CH_3NH_3Gd(SeO_4)_2$	15.93	15.93
	350	$Gd_2Se_4O_{11}$	28.31	28.71
	510	$Gd_2Se_{3.5}O_{10}$	32.47	33.61
	800	Gd_2SeO_5	59.40	58.12
Tb	200	$CH_3NH_3Tb(SeO_4)_2$	16.08	15.89
	400	$Tb_2Se_{3.5}O_{10}$	32.43	33.52
	800	Tb_2SeO_5	59.98	58.12
Ho	200	$CH_3NH_3Ho(SeO_4)_2$	16.00	15.72
	345	$Ho_2Se_4O_{11}$	27.96	28.30
	520	$Ho_2Se_3O_9$	36.70	37.98
	800	Ho_2SeO_5	58.79	57.34
Y	200	$CH_3NH_3Y(SeO_4)_2$	16.82	18.12
	500	$Y_2Se_4O_{11}$	33.07	32.63
	770	$Y_2O_{1.5}SeO_6$	61.00	60.54
	1000	Y_2SeO_5	70.80	66.12

~750°C, although the weight loss continues beyond this temperature. The weight loss up to ~800°C is found to be 1–2% higher than expected for the formation of the Ln_2SeO_5 intermediate in each case, indicating its unstable nature. The DTG curves show three peaks corresponding to this stage, whereas the DTA curves exhibit two very weak endothermic peaks, and the intermediates are probably $Ln_2Se_3O_9$ and $Ln_2Se_{1.5}O_6$. *Castro et al.* [21] have studied the thermal decomposition of rare earth selenites of the composition $Ln_2Se_4O_{11}$ (Ln = Gd, Ho, Y) and $Ln_2Se_{3.5}O_{10}$ (Ln = Sm, Eu, Tb) and have reported that these compounds are stable up to ~500°C and decompose to oxides *via* the intermediates $Ln_2Se_3O_9$ and Ln_2SeO_5. *Oppermann et al.* [22, 23] have recently carried out thermochemical investigations on the systems RE_2O_3–SeO_2 (RE = Nd and Sm) and have reported selenites of the general formula $RE_2Se_4O_{11}$, $RE_2Se_{3.5}O_{10}$, $RE_2Se_3O_9$, and $RE_2Se_{1.5}O_6$.

The TG curve of the europium compound scanned up to 1000°C shows complete decomposition to Eu_2O_3. Its DTG curve contains a peak at 935°C attributable to the decomposition of Eu_2SeO_5 to Eu_2O_3.

Table 4. Results of isothermal heating of $CH_3NH_3Sm(SeO_4)_2 \cdot 5H_2O$

T/°C	% Weight loss		% *Ln* in the residue		Composition of the residue
	calcd.	obsd.	calcd.	obsd.	
150	16.13	15.84	32.10	31.87	$CH_3NH_3Sm(SeO_4)_2$
350	34.00[a] 38.97[b]	36.64	40.80[a] 44.12[b]	42.09	$Sm_2Se_{3.5}O_{10} + Sm_2Se_3O_9$
550	58.84	59.98	65.42	64.76	Sm_2SeO_5
1000	68.78	68.52	86.23	86.01	Sm_2O_3

[a] Calculated for $Sm_2Se_{3.5}O_{10}$; [b] calculated for $Sm_2Se_3O_9$

In order to characterize the intermediates, the samarium compound was chosen as a representative. It was heated to constant weight at 150, 350, 550, and 1000°C. The resultant residues were analyzed for their samarium contents; the results of isothermal heating are given in Table 4. The loss in weight and the samarium contents of the intermediate obtained at 150°C confirm the formation of anhydrous samarium methylammonium selenate. The infrared spectrum of this residue in the range of 4000 to 400 cm^{-1} is shown in Fig. 4b. The spectrum exhibits a broad absorption with a minimum at 3180 cm^{-1} which can be assigned to stretching vibrations of NH_3^+. The shoulder appearing at 3410 cm^{-1} may be due to absorbed water. The absence of any band at ~1650 cm^{-1} and in the region of 550–750 cm^{-1} are suggestive of the removal of water of crystallization. The band appearing at 1615 cm^{-1} and that at 1491 cm^{-1} are attributable to antisymmetric NH_3^+ deformation and symmetric NH_3^+ deformation vibrations, respectively. The shoulders appearing at 1465 and 1420 cm^{-1} may be assigned to antisymmetric CH_3 deformation and symmetric CH_3 deformation vibrations. The band at ~1270 cm^{-1}

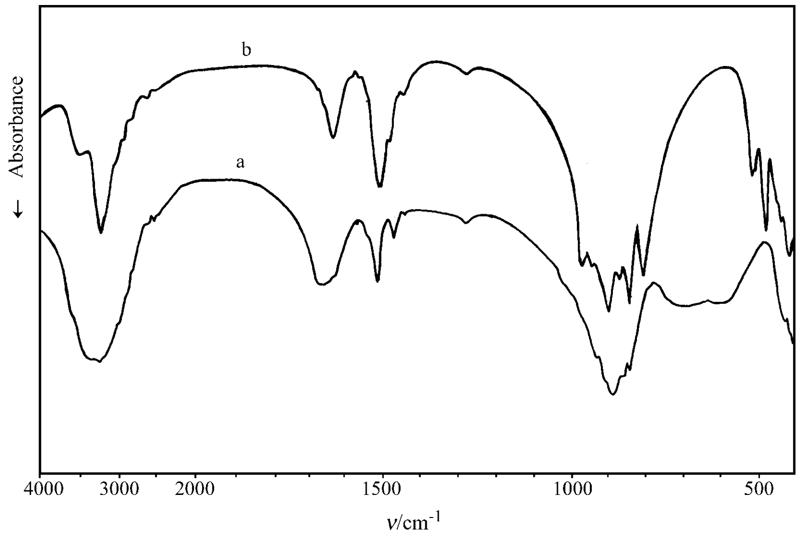

Fig. 4. IR spectra of (a) $CH_3NH_3Sm(SeO_4)_2 \cdot 5H_2O$ and (b) residue at 150°C

is due to the NH_3^+ rocking vibration. The six strong bands in the region of 980–820 cm^{-1} are due to ν_3 antisymmetric stretching vibrations, and a band at 797 cm^{-1} is due to ν_1 symmetric stretching vibrations of the selenate ions. The increase in the number of bands in this region probably suggests a lowering of the symmetry of the selenate ion when the salt gets dehydrated. The medium intensity bands below 510 cm^{-1} originate from ν_4 antisymmetric bending vibrations.

The infrared spectra of the samarium compound heated at 350, 550, and 1000°C showed no characteristic bands for NH_3^+ and CH_3, thus confirming the removal of monomethylammonium selenate. These spectra are shown in Fig. 5. The loss in weight at 350°C and the samarium contents of the corresponding residue adopt values intermediate between those calculated for $Sm_2Se_{3.5}O_{10}$ and $Sm_2Se_3O_9$. The infrared spectrum (Fig. 5a) shows two very broad bands with minima at ~900 and ~720 cm^{-1}. Comparison of this spectrum with the spectra of selenites of various compositions reported by *Oppermann et al.* [22] also suggests that the product at 350°C is most probably a mixture of $Sm_2Se_{3.5}O_{10}$ and $Sm_2Se_3O_9$. However, the reported spectra of both compounds exhibit six to seven bands in the range of 900–600 cm^{-1} which are not resolved in the present case. The band at ~900 cm^{-1} disappears upon heating the compound to 550°C; a broad band centered around 720 cm^{-1} with a shoulder at ~830 cm^{-1} is indicative of the presence of Sm_2SeO_5 (Fig. 5b). The weight loss and the samarium contents of the intermediate also confirm these observations. Finally, the weight loss observed at

Fig. 5. IR spectra of (a) residue at 350°C, (b) residue at 550°C, (c) residue at 1000°C

1000°C and the samarium contents of the respective product correspond to the formation of Sm_2O_3. The infrared spectrum of this final product (Fig. 5c) is typical of samarium oxide.

Experimental

An aqueous solution of monomethylammonium selenate (*MMAS*) was obtained by adding an aqueous solution of selenic acid ($\sim 1N$) to an aqueous methylamine solution in stoichiometric amounts. The aqueous solutions of rare earth selenate and *MMAS* were mixed in molar ratios of *Ln*:*MMAS* = 1:1 to 1:5. The resultant mixture was concentrated to a small volume (5–8 cm^3) on a steam bath in each case. Dry EtOH was added to this solution after it attained room temperature. The precipitated product was filtered, washed with 95% EtOH, and dried over P_2O_5. The rare earth contents of the products were determined complexometrically, selenate contents gravimetrically as $PbSeO_4$. The percentage of nitrogen was determined by the micro-*Dumas* method.

The TG curves of the compounds were obtained on a TA instrument under N_2; the DTA curves were recorded on a DuPont instrument model 1600 under N_2. A heating rate of 20°C/min was employed. The DTA curves were scanned using alumina crucibles and Al_2O_3 as reference. The infrared spectra were scanned in the range 4000–400 cm^{-1} on a Shimadzu FTIR-4200 spectrophotometer using the KBr disk technique. The X-ray powder diffractograms of the compounds were obtained using a Jeol powder diffractometer.

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