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Studies on selenates XIII:[1] Synthesis and crystal chemical characterisation of $K_3Ln(SeO_4)_3.nH_2O$

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Abstract

The double selenates with the general formula $K_3Ln(SeO_4)_3.nH_2O$ (Ln=La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Yb and Y) have been prepared from the aqueous medium by crystallisation technique at room temperature. The compounds exhibit various degrees of hydration. X-ray powder diffraction and IR spectroscopy have been utilized for their structural characterisation. From the X-ray data the selenate hydrates appear to form more than one group of isomorphous series. The major assignments of the vibrational bands have been made and the results are discussed.

Keywords: Selenates; Lanthanides; X-ray diffraction; Infra-red

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Table 1
Crystal data for $K_3Ln(SeO_4)_3.nH_2O$

Lanthanide	n	a (pm)	b (pm)	c (pm)	β (°)	$v \times 10^{-6}$ (pm^3)	d calc. $mg\ m^{-3}$	d obs. $mg\ m^{-3}$
La	0.50	965 ±	1022 ±	1274 ±	90.71 ±0.16	1256	3.67	3.70 ±0.01
Ce	0.50	962 ±2	1020 ±2	1277 ±4	90.45 ±0.20	1254	3.68	3.73 ±0.01
Pr	0.50	963 ±2	1018 ±1	1279 ±2	90.53 ±0.10	1254	3.69	3.75 ±0.01
Nd	0.50	964 ±1	1021 ±2	1270 ±2	91.15 0.33	1250	3.72	3.74 ±0.01
Dy	1.00	1591 ±2	870 ±1	964 ±1	94.30 ±0.10	1330	3.63	3.61 ±0.02
Ho	1.00	1576 ±2	865 ±1	963 ±1	94.17 ±0.09	1309	3.70	3.65 ±0.01
Er	1.00	1572 ±2	865 ±1	962 ±1	94.16 ±0.08	1305	3.73	3.71 ±0.01
Gd	1.25	1458 ±1	697 ±1	1285 ±‘	91.44 ±0.09	1305	3.70	3.67 ±0.01
Tb	1.25	1456 ±2	697 ±1	1281 ±1	91.34 ±0.09	1300	3.72	3.69 ±0.01
Yb	1.25	1447 ±3	701 ±1	1280 ±2	91.28 ±0.20	1298	3.77	3.72 ±0.02
Y	1.25	1451 ±2	697 ±2	1281 ±2	91.58 ±0.15	1296	3.34	3.28 ±0.02

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[1] Studies on Selenates XII: Reference [10].

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1. Introduction

The many investigations of rare earth containing alkali double chalcogenate hydrates have resulted in synthesis and characterisation of numerous compounds [1–10]. The present work describes the spectrostructural studies of the double selenates with the general formula $K_3Ln(SeO_4)_3.nH_2O$ where Ln is lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium or yttrium.

1.1. Experimental

The double selenates $K_3Ln(SeO_4)_3.nH_2O$ were prepared by crystallisation from the aqueous solutions containing the required proportion of potassium and rare earth selenates at room temperature. The crystallised products were chemically analysed following standard methods [11]. Lanthanides were analysed complexometrically, potassium flame photometrically and selenate by acidimetric titrations after eluting aqueous solutions of the double selenates through a cation exchange column packed with a resin Dowex 50X8. The water contents were normally evaluated by differences and were confirmed in representative cases by thermogravimetry and differential thermogravimetry. The structural analysis was carried out using X-ray powder diffractometer Model No. PW 1009/30 NRD 1023 using nickel filter copper radiations. The infra-red absorption spectra were scanned in the range 2000–200 cm^{-1} on a Beckman IR 4250 spectrophotometer using CsBr pellet technique.

2. Results and discussion

The chemical analysis [12] indicates that the double selenates $K_3Ln(SeO_4)_3.nH_2O$ crystallise out in three

Table 2
Indexed X-ray powder diffraction pattern for $K_3Pr(SeO_4)_3.0.5H_2O$

h	*k*	*l*	*d* calc. (pm)	*d* obs. (pm)	I/I_O
1	1	0	700	701	16
2	0	0	482	482	5
2	0	1	449	448	16
1	2	$\bar{2}$	369	368	5
2	1	$\bar{2}$	349	348	16
3	0	0	321	321	100
0	1	4	305	306	6
1	3	2	286	286	50
0	3	3	265	264	10
3	0	$\bar{3}$	258	257	4
1	4	3	213	214	17
0	5	2	193.9	194.1	18
5	0	$\bar{3}$	176.2	176.1	3
3	5	$\bar{1}$	171.4	171.2	11
4	2	5	165.1	165.1	4
6	0	0	160.6	160.7	3

Table 3
Indexed X-ray powder diffraction pattern for $K_3Er(SeO_4)_3.H_2O$

h	*k*	*l*	*d* calc. (pm)	*d* obs. (pm)	I/I_O
0	1	0	865	864	23
2	0	0	784	785	24
2	1	$\bar{1}$	509	510	4
0	0	2	480	480	4
3	1	0	447	447	7
3	1	1	396	396	5
4	0	$\bar{1}$	372	372	13
2	2	1	348	348	38
3	0	2	341	341	12
3	2	0	333	334	11
0	0	3	320	320	100
1	0	3	309	309	14
0	1	3	300	300	35
2	1	$\bar{3}$	287	288	48
3	2	$\bar{2}$	280	279	20
2	3	0	271	271	19
3	1	$\bar{3}$	268	268	4
3	0	3	265	265	15
3	3	0	252	252	6
3	2	3	226	226	9
4	0	$\bar{4}$	212	213	12
5	2	$\bar{3}$	205	205	10
8	1	0	197.6	197.2	8
7	1	2	192.7	193.3	10
7	2	$\bar{2}$	188.1	188.5	9

Table 4
Indexed X-ray powder diffraction pattern for $K_3Tb(SeO_4)_31.25H_2O$

h	*k*	*l*	*d* calc. (pm)	*d* obs. (pm)	I/I_O
0	1	0	697	702	29
0	0	2	640	639	14
1	0	$\bar{2}$	591	588	15
1	1	1	548	548	9
3	0	0	485	485	5
3	0	1	450	451	5
1	0	$\bar{3}$	412	412	4
3	1	0	398	398	6
3	1	1	378	379	3
4	0	0	364	364	14
1	1	$\bar{3}$	355	354	13
0	2	0	339	339	3
3	1	2	335	334	3
0	0	4	320	323	100
3	0	3	317	316	15
2	2	1	305	303	2
1	2	$\bar{2}$	300	300	1
1	2	2	299	298	2
5	0	0	291	292	4
3	1	3	288	288	18
1	1	$\bar{4}$	284	284	16
4	0	3	274	274	5
5	1	0	269	268	4
1	0	$\bar{5}$	253	253	4
4	2	3	215	215	9
7	1	0	199.3	199.3	4
6	2	$\bar{2}$	191.2	191.3	6
5	1	5	183.4	184.0	5

Table 5
Infra-red frequencies in cm^{-1} for $K_3Ln(SeO_4)_3.nH_2O$

K_3 $Pr(SeO_4)_3 0.5H_2O$	$K_3Er(SeO_4)_3.H_2O$	$K_3Tb(SeO_4)_3 1.25H_2O$	Assignment
	1720 m		$\nu_2(H_2O)$
1635 m	1635 s	1620 s	
		1605s	
	940 m, sh	932 m, sh	$\nu_3(SeO_4)$
925 v, wsh	926 w, sh		
900 vs	910 vs	902 vs	
870 s, sh	880 vs	882 w	
865 v, wsh	862 vs	868 m	
830 s	840 s	838 m, sh	$\nu_1(SeO_4)$
	823 m	825 s	
	810 w	800 m, sh	
755 w, sh		755 w	Ln–OH_2 rocking
728 w	725 m	735 w	
692 w		698 w	
		682 w	
		665 w	
561 m, sh			Ln–OH_2 wagging
530 m, sh			
	480 m	480 sh	$\nu 1(SeO_4)$
		450 sh	
432 m, sh	437 m, sh	435 s	
	418 sh	418 sh	
400 s	400 s	395 s	
378 m, sh			$\nu 2(SeO_4)$
368 m, sh		358 vs	
332 m, sh	340 m	338 m, sh	
312 m, sh		310 sh	

m, medium; s, strong; sh, shoulder; v, very; w, weak.

groups of compounds varying in degrees of hydration. The first group containing La, Ce, Pr, and Nd double selenates are hemihydrates, the second comprising of Dy, Ho and Er are monohydrates and the third having Gd, Tb, Yb and Y crystallise with one and a quarter molecules of hydrate water.

The X-ray diffraction patterns confirm the isostructurality within these groups. All the reflections in the patterns of each group can be indexed in the distinctly different monoclinic system each containing four molecules per unit cell. The least squares refined unit cells parameters and experimental and calculated densities of the members of these groups are given in Table 1. The interplanar d spacing and the observed intensities I/I_0 for the representative member of the three groups are included in Table 2, Table 3 and Table 4.

The X-ray diffraction data of the monohydrate group $K_3Ln(SeO_4)_3.H_2O$ (Ln=Dy, Ho, Er) appear so far as the intense reflexes are concerned to be comparable with the published unindexed data on potassium lanthanide chromium oxide hydrate $K_3Ln(CrO_4)_3.H_2O$ (Ln=Pr, Nd, Sm, Eu, Gd) [13] suggesting possible isotypism.

The profiles of the infra-red spectra of the double selenates of the three groups are similar amongst its members. In the absence of the knowledge of the correct space group for want of single crystal studies, the detailed site and factor group analysis are not attempted. However the number and the positions of the bands are suggestive of lowering the ideal tetrahedral symmetry of the selenate group. The symmetry of the selenate group seems to be lowered to an extent, effectively resulting in the activation of all the infra-red inactive bands and complete removal of degeneracies of the degenerate bands. The assignments of the spectral bands of the members of each group are done by comparison with the earlier reported data on the double selenates [14,15]. The spectral data with the band assignment for the representative member of each group are given in Table 5.

Interestingly, the bending vibration of the water molecule appears as a doublet in the spectra of monohydrates and one and a quarter hydrates suggesting possibly their bonding in more than one way in these double selenates.

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