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INFRARED AND X-RAY MEASUREMENTS ON VARIOUS INORGANIC ION EXCHANGERS

L. ZSINKA, L. SZIRTES and J. MINK

Institute of Isotopes, Hungarian Academy of Sciences, Budapest (Hungary)

and

A. KÁLMÁN

Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest (Hungary)

SUMMARY

Investigations were carried out on crystalline cerium phosphate and arsenate in the lithium, sodium, potassium and caesium forms. The various salt forms were prepared according to the results obtained in ion uptake measurements. It was found that the water loss up to 150° is about one mole of water of crystallization. The bands belonging to structural water decrease with increase in the alkali metal content.

The stretching frequencies are characteristic of HAsO_4^{3-} and PO_4^{3-} groups, changing according to the ionic radii, *i.e.*, samples with different alkali metal contents have different structures.

INTRODUCTION

Investigations have been carried out on crystalline cerium arsenate and phosphate in the lithium, sodium, potassium, rubidium and caesium forms, and the results obtained with these samples are discussed in this paper. The samples were synthesized according to Alberti *et al.*¹. The X-ray and IR measurements were carried out as described elsewhere². The cerium content of the samples was determined by the method of Greenhous *et al.*³, the alkaline metal content with flame photometry.

RESULTS AND DISCUSSION

The ion uptake results for different forms of the ion exchangers are shown in Fig. 1. These results are in good agreement with those obtained analytically and calculated from the weight losses (Table I). According to these results, most of the samples were dried at 150° for the further investigations.

Based on the analytical measurements performed, the following compositions have been calculated:

CeAs-H	$\text{Ce}(\text{HAsO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ main product
CeAs-Li/1	$\text{Ce}(\text{Li}_{0.37} \text{H}_{0.60} \text{AsO}_4)_2 \cdot 1.10\text{H}_2\text{O}$
CeAs-Li/2	$\text{Ce}(\text{Li}_{0.65} \text{H}_{0.39} \text{AsO}_4)_2 \cdot 0.67\text{H}_2\text{O}$
CeAs-Na/1	$\text{Ce}(\text{Na}_{0.40} \text{H}_{0.64} \text{AsO}_4)_2 \cdot 0.60\text{H}_2\text{O}$

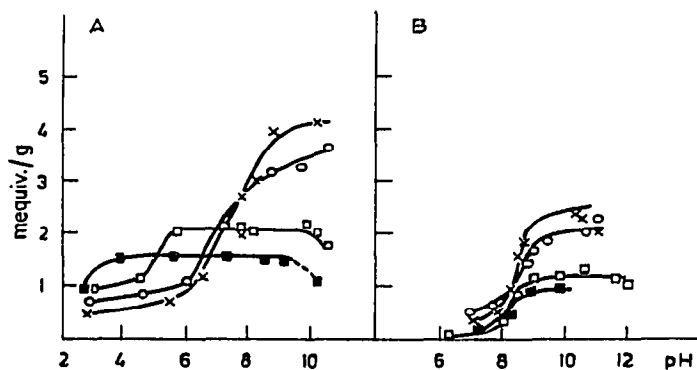


Fig. 1. Ion uptake curves: \times , Li^+ ; \circ , Na^+ ; \square , K^+ ; \blacksquare , Cs^+ . A, Cerium arsenate; B, cerium phosphate.

TABLE I
WEIGHT LOSSES AT VARIOUS TEMPERATURES

Sample	Weight losses (%)		
	150°	200°	400°
CeAs-H	0	2.10	4.20
CeAs-Li/1	2.20	4.59	6.53
CeAs-Li/2	—	2.82	4.53
CeAs-Na/1	1.08	2.57	5.41
CeAs-Na/2	0.31	0.43	0.51
CeAs-K/1	1.10	2.59	5.46
CeAs-Rb/1	1.16	2.60	5.90
CeAs-Cs/1	1.20	2.63	6.10
CeP-H	1.60	2.50	7.20
CeP-Li/1	1.40	2.63	4.30
CeP-Li/2	1.30	2.50	3.64
CeP-Na/1	1.80	3.60	4.95
CeP-K/1	1.61	3.08	6.10

TABLE II
FIRST INTERPLANAR DISTANCES

Sample	d (Å)	Sample	d (Å)	Sample	d (Å)
CeAs-H (25°)	9.25	CeAs-Li/2 (25°)	8.67	CeP-H (25°)	15.39
CeAs-Li/1 (25°)	8.92	CeAs-Li/2 (150°)	8.40	CeP-Li/1 (25°)	14.72
CeAs-Li/1 (150°)	7.97	CeAs-Na/2 (25°)	10.62	CeP-Li/1 (150°)	14.48
CeAs-Na/1 (25°)	8.33	CeAs-Na/2 (150°)	9.26	CeP-Na/1 (25°)	14.48
CeAs-Na/1 (150°)	9.02	CeAs-K/2 (25°)	—	CeP-Na/1 (150°)	14.06
CeAs-K/1 (25°)	8.76	CeAs-K/2 (150°)	—	CeP-K/1 (25°)	14.22
CeAs-K/1 (150°)	8.67	CeAs-Rb/1 (25°)	—	CeP-K/1 (150°)	13.80
CeAs-Rb/1 (25°)	8.96	CeAs-Cs/1 (25°)	—		
CeAs-Cs/1 (25°)	9.28				

CeAs-Na/2	$\text{Ce}(\text{Na}_{0.99} \text{H}_{0.01} \text{AsO}_4)_2 \cdot 0.10\text{H}_2\text{O}$
CeAs-K/1	$\text{Ce}(\text{K}_{0.43} \text{H}_{0.06} \text{AsO}_4)_2 \cdot 0.76\text{H}_2\text{O}$
CeAs-Rb/1	$\text{Ce}(\text{Rb}_{0.28} \text{H}_{0.70} \text{AsO}_4)_2 \cdot 0.87\text{H}_2\text{O}$
CeAs-Cs/1	$\text{Ce}(\text{Cs}_{0.23} \text{H}_{0.75} \text{AsO}_4)_2 \cdot 0.90\text{H}_2\text{O}$
CeP-H	$\text{Ce}(\text{HPO}_4)_2 \cdot 0.33\text{H}_2\text{O}$ main product
CeP-Li/1	$\text{Ce}(\text{Li}_{0.6} \text{H}_{0.4} \text{PO}_4)_2 \cdot 0.27\text{H}_2\text{O}$
CeP-Li/2	$\text{Ce}(\text{Li}_{0.75} \text{H}_{0.25} \text{PO}_4)_2 \cdot 0.25\text{H}_2\text{O}$
CeP-Na/1	$\text{Ce}(\text{Na}_{0.57} \text{H}_{0.43} \text{PO}_4)_2 \cdot 0.35\text{H}_2\text{O}$
CeP-K/1	$\text{Ce}(\text{K}_{0.22} \text{H}_{0.78} \text{PO}_4)_2 \cdot 0.31\text{H}_2\text{O}$

In Tables II-IV the X-ray data are collected. The data indicate that all the samples examined are crystalline. After heating to 150° , because of the loss of water, the lattices shrunk, which can be followed by comparing the first interplanar distances of the corresponding samples in Table II.

The results of the infrared (IR) investigations and conclusions that can be drawn concerning the structure are discussed below.

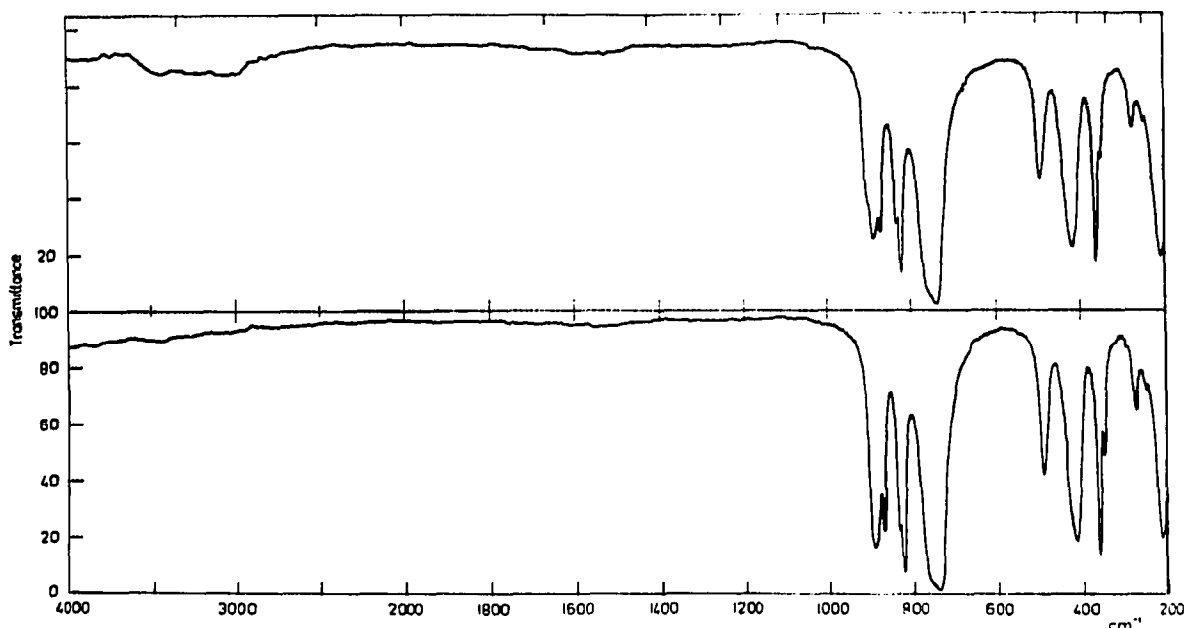


Fig. 2. IR spectra of cerium arsenate in the sodium form. 1, CeAs-Na/2 (25°); 2, CeAs-Na/2 (150°).

In Fig. 2 the IR spectra of arsenates in sodium form (normal and heated to 150°) are shown as an example. When the sample is heated, the band width decreases, giving a more definite band separation which, in accordance with X-ray data, indicates a higher degree of crystallinity. The above change in crystalline structure could be ascribed to the decrease in the water content of the sample, which is demonstrated by decreasing band intensities of molecular water at about 3600 and 1640 cm^{-1} .

The IR spectra of samples containing different amounts of alkali metals indicate that the relative band intensities (at about 2950 , 2340 and 1200 cm^{-1}) decrease

TABLE III

DATA FROM X-RAY MEASUREMENTS AT 25°

Abbreviations: vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

<i>CeAs-H</i>	<i>CeAs-Li/1</i>	<i>CeAs-Li/2</i>	<i>CeAs-Na/1</i>	<i>CeAs-Na/2</i>	<i>CeAs-K/1</i>	<i>CeAs-Rb/1</i>	<i>CeAs-Cs/1</i>
—	—	—	9.18 vw	—	11.18 vw	—	—
—	—	—	—	—	9.61 vw	—	—
9.25 vs	8.92 vs	8.67 vs	8.33 vs	10.62 vs	8.76 vs	8.96 vs	9.28 vs
—	8.19 w	—	—	9.24 w	—	—	—
3.80 w	—	—	—	3.95 vw	—	—	—
3.75 vw	—	—	—	—	—	—	—
—	—	3.60 vw	3.66 w	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	3.33 vw	—	—	—	—	3.33 w
—	3.29 w	—	—	—	—	3.28 w	—
—	—	—	—	3.24 w	3.23 w	—	—
—	—	—	—	3.18 w	—	—	—
—	—	—	—	—	3.10 w	3.10 w	3.12 m
3.09 m	3.09 w	3.06 w	3.08 w	3.06 w	—	3.06 w	3.07 w
—	—	—	—	—	3.02 vw	—	—
2.94 w	—	—	—	—	2.94 w	—	—
—	—	—	2.90 w	2.91 vw	2.92 vw	—	—
—	—	—	2.72 vw	—	—	—	—
—	—	—	—	2.68 m	—	—	—
—	—	—	—	2.57 w	—	—	—
2.46 w	—	—	—	—	2.49 vw	—	—
2.43 vw	—	—	—	2.45 vw	—	2.41 vw	2.59 vw
—	—	—	—	—	—	—	—
2.31 w	—	—	—	—	—	—	—
—	—	—	2.28 vw	2.23 vw	2.18 vw	—	—
2.05 vw	2.04 vw	—	2.04 vw	—	2.05 vw	2.05 vw	2.05 vw
<hr/>							
<i>CeP-H</i>	<i>CeP-Li/1</i>	<i>CeP-Li/2</i>	<i>CeP-Na/1</i>	<i>CeP-Na/2</i>	<i>CeP-K/1</i>	<i>CeP-Rb/1</i>	<i>CeP-Cs/1</i>
—	—	—	—	—	14.67 m	—	—
15.39 vs	14.72 vs	—	14.48 vs	—	14.22 vs	—	—
7.86 m	—	—	—	—	—	—	—
—	7.34 w	—	7.30 w	—	7.31 m	—	—
—	—	—	—	—	—	—	—
—	6.41 vw	—	—	—	—	—	—
—	—	—	—	—	5.95 vw	—	—
5.54 w	5.54 vw	—	—	—	—	—	—
5.26 m, s	—	—	—	—	—	—	—
—	4.88 m	—	4.87 m	—	—	—	—
—	—	—	4.69 vw	—	—	—	—
4.43 m	—	—	—	—	4.59 m	—	—
—	—	—	—	—	—	—	—
3.95 s	—	—	—	—	3.99 vw	—	—
3.66 w	3.65 m	—	3.66 m, s	—	3.66 m, s	—	—
—	—	—	3.51 vw	—	—	—	—
3.41 m	3.41 vw	—	3.40 vw	—	3.42 vw	—	—
—	—	—	—	—	—	—	—
—	3.29 vw	—	—	—	—	—	—
3.16 m	—	—	—	—	—	—	—
3.10 vw	—	—	—	—	—	—	—
2.94 m	2.95 vw	—	2.92 vw	—	2.94 vw	—	—
—	—	—	—	—	2.87 vw	—	—
2.71 vw	—	—	—	—	—	—	—
2.64 vw	—	—	—	—	—	—	—
—	2.43 w	—	—	—	2.44 w	—	—

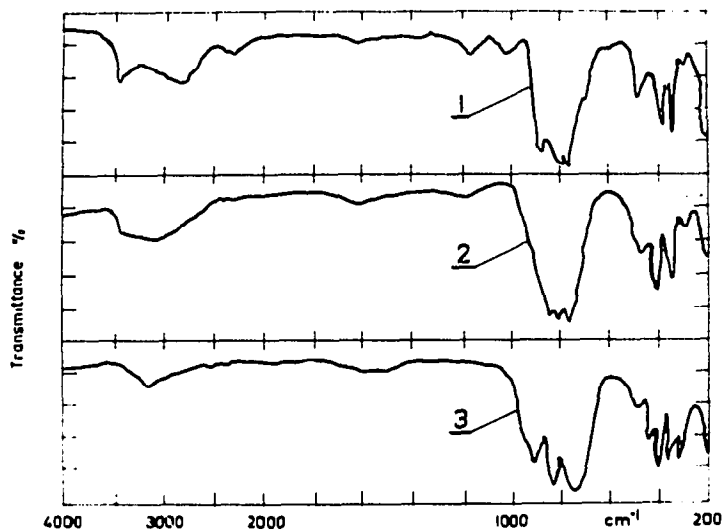


Fig. 3. IR spectra of cerium arsenate in the hydrogen and lithium forms. 1, CeAs-H; 2, CeAs-Li/1; 3, CeAs-Li/2.

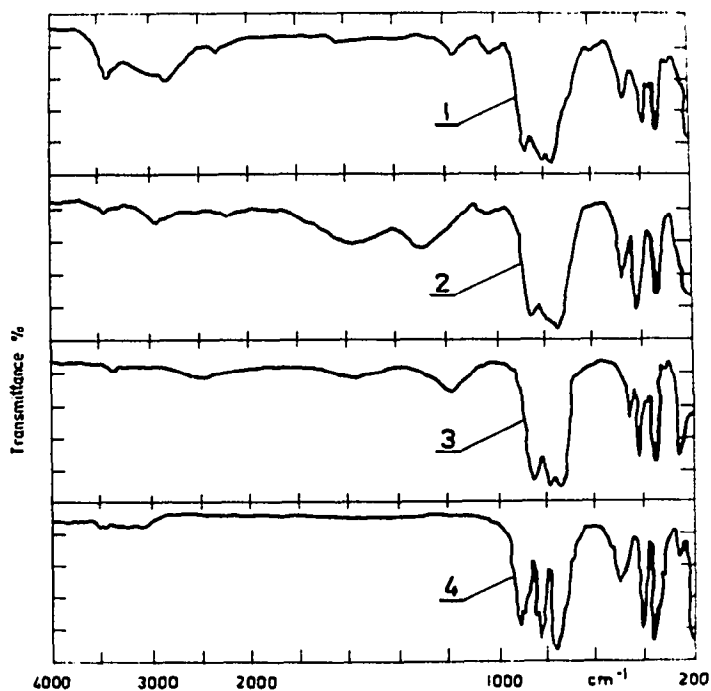


Fig. 4. IR spectra of cerium arsenate in the hydrogen, potassium and sodium forms. 1, CeAs-H; 2, CeAs-K/1; 3, CeAs-Na/1; 4, CeAs-Na/2.

proportionally with increasing alkali metal content of the sample, as is shown for the Li^+ form of cerium arsenate in Fig. 3. The relative intensity of the bands assigned to AsO_4^{3-} groups becomes more characteristic with increasing Li^+ content. This IR pattern unambiguously verified the H^+ exchange of the acidic HAsO_4^{2-} groups.

Comparison of the spectra of samples assigned under $\text{Me}^+/1$ (Fig. 4) indicates that these materials have a similar type of lattice. In the spectra of all samples, bands relating to acidic HAsO_4^{2-} groups (3000 , 2320 , 1300 – 1200 and 1050 cm^{-1}) can be found. If the alkali metal content approaches the total capacity value, these frequencies virtually disappear and only the bands relating to water of crystallization evaporating at 150° (3150 and *ca.* 1600 cm^{-1}) are visible.

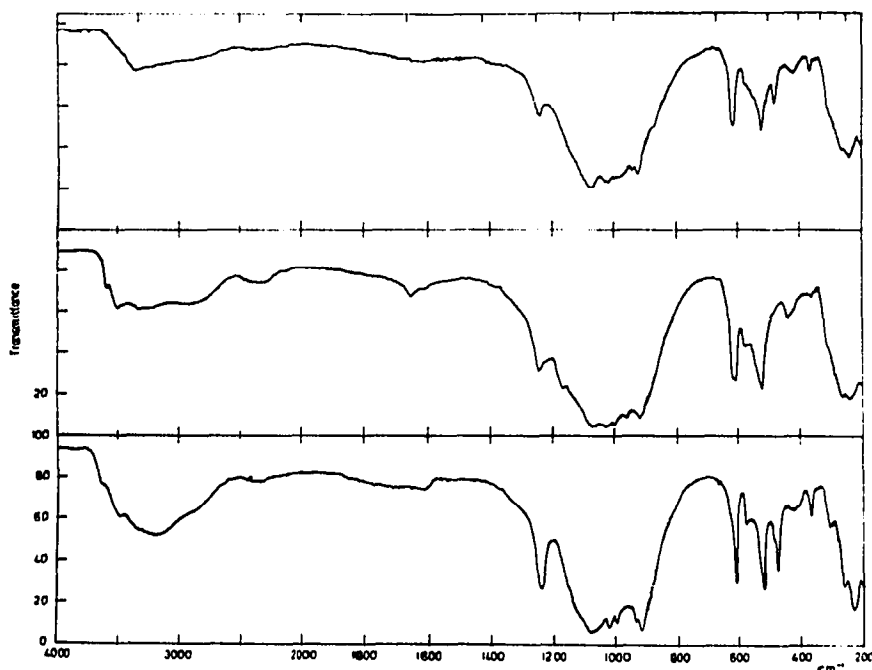


Fig. 5. IR spectra of cerium phosphate in the hydrogen and sodium forms. 1, CeP-H; 2, CeP-Na/1 (25°); 3, CeP-Na/1 (150°).

The IR spectra of cerium phosphates are shown in Fig. 5. The bands assigned to acidic HPO_4^{2-} groups (2350 and 1230 cm^{-1}) were established. Comparing the IR spectroscopic behaviour of cerium arsenates and phosphates, similar conclusions can be drawn. The decreasing intensities of HPO_4^{2-} bands according to the alkali metal content and the considerable water loss at 150° in the Na^+ form cerium phosphate can be seen in Fig. 5 (see the bands at 3500 and 1650 cm^{-1}). It may be noticed that sodium–hydrogen exchange is less stoichiometric than those with cerium arsenate (see the band at 1240 cm^{-1}). The influence of the alkali metal cation content on the IR spectra of arsenates and phosphates has been investigated and the characteristic bands are given in Table V.

It can be seen from Table V that the stretching frequencies of As–O at about

TABLE V
FREQUENCY DATA

Species	Frequency					
CeAs-Me ⁺ /1	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>	} As-O stretching
	850 w	840 w	845 w	848 w	848 w	
	760 vs	790 vs	765 vs	785 vs	784 vs	} O-As-O deformation
		750 vs				
	470 w	482 w	478 w	481 w	476 w	
	408 w	416 w	416 w	418 w	413 w	
	354 w, m	347 w, m	350 w, m	350 w, m	344 w, m	
260 m	220 m	~200 m	~200 m	~200 m	Lattice vibration	
CcAs-Me ⁺ /2	<i>Li</i>	<i>Na</i>				} As-O stretching
	921 m	892 m				
	896 w	870 w				
	825 m	822 m				
	740 vs	752 vs				Lattice vibration
	420 m	418 m				
	370 w	364 w				
326 m	275 m					
CeP-Me ⁺ /1	<i>Li</i>	<i>Na</i>	<i>K</i>			
	1035 vs	1065 vs	1070 vs			
		1025 m	1020 m			
	915 vs	915 vs	915 vs			
	600 m	610 m	610 m			
	520 m, w	518 m	518 m			
	455 vw	480 w	472 m			
	421 vw	430 w	418 w			
	370 vw	365 w	364 w			
250 m	240 m	232 m				

760 cm⁻¹ and P-O at about 1060 cm⁻¹, characteristic of AsO₄³⁻ and PO₄³⁻ groups, respectively, changed as the ionic radii varied; at the same time, the lattice vibrations (200–260 cm⁻¹) decrease, probably because of the increase in the distance between the anions. The other frequencies can probably be assigned to such types of AsO₄³⁻ and PO₄³⁻ vibrational forms that have no influence on the cation-anion interaction. The crystal lattice interaction should decrease, *i.e.*, we approach nearer to the fundamental frequencies of "free" anionic groups (having no perturbation). The above consideration seems to be true for the samples marked Me⁺/2 (arsenates), and it is evident from the character of the spectra that the completely saturated samples should have a different crystalline structure.

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