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The substitution of cations by magnesium in the structure $K_3Ho(VO_4)_2$

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Abstract

The cation substitutions in the crystal lattice of binary potassium–holmium vanadate (V) $K_3Ho(VO_4)_2$ by magnesium have been studied using various types of chemical solid state reactions. It was shown that in the presence of the quasi-ternary system K_3VO_4–$Mg_3(VO_4)_2$–$HoVO_4$ at 700°C there a compound defined as $K_3Ho(VO_4)_2$ with a narrow homogeneity range where K and Ho are partially substituted by Mg in accordance with various schemes. © 1998 Published by Elsevier Science S.A.

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1. Introduction

A number of inorganic compounds have been prepared by substitution of the elements in the matrix $M_nLn_m(TO_4)_l$, where M is an alkaline metal, Ln is a rare earth element, T is P, As, V, Cr etc [1–4]. The series of binary compounds $M_3Ln(TO_4)_2$ is characterised by a layer network belonging to structural types of glazerite or of β-K_2SO_4, the latter closely related to $K_3Na(SO_4)_2$ [5]. These structural features are preserved even in the case of the simultaneous presence of two different alkaline cations and two related anionic tetrahedral groups, e.g. PO_4 and VO_4 [6]. In the substitution of alkaline cation M for alkaline-earth cation M′ in the compounds $M_3Ln(TO_4)_2$, the compounds $MM'Ln(TO_4)_2$ (M=Na) were obtained [7,8] belonging to structural type palmierite $K_2Pb(SO_4)_2$ [9]. No information on this type of compound containing magnesium has been available so far. The purpose of the present research is the possibility of magnesium (and some of the alkaline earths) introduction into the $K_3Ho(VO_4)_2$ structure, in accordance with the following substitution schemes: $2K^+ \Rightarrow Mg^{2+}$; $2Ho^{3+} \Rightarrow 3Mg^{2+}$; and $K^+ + Ho^{3+} \Rightarrow 2Mg^{2+}$.

2. Experimental

X-ray diffraction studies were carried out using a DRON-3M Diffractometer (Co Kα radiation). The software ‘Roentgen EXE’ was employed for the phase identifications and refinements of crystal lattice parameters. Thermogravimetric studies (heating and cooling curves) have been used both to determine phase diagram liquidus lines and reveal solid state phase transitions.

Analysis was carried out in Pt holders in air using a Q1500D Derivatograph. Sample masses were up to 300 mg; heating rate up to 15°C min^{-1}. The IR spectra were recorded by Spectrophotometers UR-20 and PE FTIR1600; Nujol and hexachlorbutadiene were used to prepare suspensions.

A series of vanadates corresponding to the general compositions: $K_{3-2x}Mg_x(VO_4)_2$ $(0.05 \leq x \leq 1.0)$, $K_3Mg_xHo_{1-0.667x}(VO_4)_2$ $(0.1 \leq x \leq 1.0)$ and $K_{3-x}Mg_{2x}Ho_{1-x}(VO_4)_2$ $(0.05 \leq x \leq 0.9)$ were obtained by solid state reactions involving potassium carbonate, holmium, magnesium and vanadium (v)oxides as precursors. Furthermore, additional compositions were synthesized in order to study phase relationships at 700°C between the components of the quasi-ternary system K_3VO_4–$Mg_3(VO_4)_2$–$HoVO_4$(Fig. 1). The compositions of the samples studied are given in Tables 1 and 2,2.

As was revealed by IR spectroscopic controls in previous tests, straightforward dynamic heatings (~10 grad min^{-1}) are inappropriate, since total CO_2 elimination from the mixtures cannot be attained, at least in the temperature range of 200–800°C. In order to assure the reproducibility of phase formation and to avoid undesirable losses of V_2O_5, a multi-step heating program has been worked out. Quasi-isothermal programming used in stepwise treatments was as following: 200, 300, 500, 600 and

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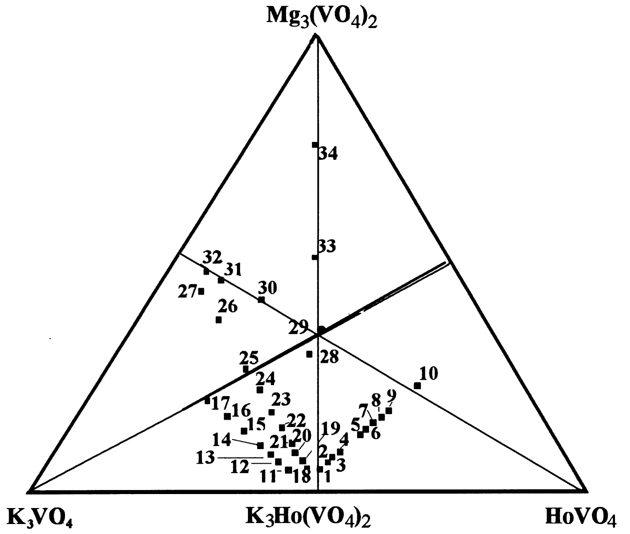

Fig. 1. Composition of the samples studied in the system K_3VO_4–$HoVO_4$–$Mg_3(VO4)_2$.

Table 1
Compositions of the samples obtained following the substitutions $2K^+ \Rightarrow Mg^{2+}$; $2Ho^{3+} \Rightarrow 3Mg^{2+}$ and $K^+ + Ho^{3+} \Rightarrow 2Mg^{2+}$ in $K_3Ho(VO_4)_2$

Sample	Composition, at. fractions			Ho containing
	K	Mg	Ho	phases
$2K^+ \Rightarrow Mg^{2+}$				
1	2.9	0.05	1	$K_3Ho(VO_4)_2$ $HoVO_4$
2	2.8	0.10	1	$K_3Ho(VO_4)_2$ $HoVO_4$
3	2.7	0.15	1	$K_3Ho(VO_4)_2$ $HoVO_4$
4	2.5	0.25	1	$K_3Ho(VO_4)_2$ $HoVO_4$
5	2.0	0.5	1	$K_3Ho(VO_4)_2$ $HoVO_4$
6	1.8	0.60	1	$K_3Ho(VO_4)_2$ $HoVO_4$
7	1.7	0.65	1	$K_3Ho(VO_4)_2$ $HoVO_4$
8	1.6	0.70	1.	$K_3Ho(VO_4)_2$ $HoVO_4$
9	1.5	0.75	1	$K_3Ho(VO_4)_2$ $HoVO_4$
10	1.0	1.0	1.0	$HoVO_4$
$2Ho^{3+} \Rightarrow 3Mg^{2+}$				
11	3.0	0.1	0.933	$K_3Ho(VO_4)_2$
12	3.0	0.2	0.867	$K_3Ho(VO_4)_2$
13	3.0	0.3	0.800	$K_3Ho(VO_4)_2$
14	3.0	0.4	0.733	$K_3Ho(VO_4)_2$
15	3.0	0.6	0.600	$K_3Ho(VO_4)_2$
16	3.0	0.8	0.467	$K_3Ho(VO_4)_2$
17	3.0	1.0	0.333	$K_3Ho(VO_4)_2$
$K^+ + Ho^{3+} \Rightarrow 2Mg^{2+}$				
18	2.95	0.1	0.95	$K_3Ho(VO_4)_2^{*}$)
19	2.9	0.2	0.9	$K_3Ho(VO_4)_2^{*}$)
20	2.85	0.3	0.85	$K_3Ho(VO_4)_2^{*}$)
21	2.8	0.4	0.8	$K_3Ho(VO_4)_2$ $HoVO_4$
22	2.7	0.6	0.7	$K_3Ho(VO_4)_2$ $HoVO_4$
23	2.6	0.8	0.6	$K_3Ho(VO_4)_2$ $HoVO_4$
24	2.5	1.0	0.5	$K_3Ho(VO_4)_2$ $HoVO_4$
25	2.4	1.2	0.4	$K_3Ho(VO_4)_2$ $HoVO_4$
26	2.2	1.6	0.2	$HoVO_4$
27	2.1	1.8	0.1	$HoVO_4$

T=700°C

[b] Single-phase region.

Table 2
Composition of the phases with high contents in Mg3$(VO_4)_2$

Sample	Composition, mol. fractions		
	K_3VO_4	$Mg_3(VO_4)_2$	$HoVO_4$
28	35	30	35
29	33.3	33.3	33.3
30	40	40	20
31	45	45	10
32	46.5	46.5	7
33	25	50	25
34	12.5	75	12.5

700°C. For the best crystallisation of the phases the temperature, in some cases, was raised up to 800°C.

3. Results and discussion

In accordance with the data in Tables 1 and 2, the compound $K_3Ho(VO_4)_2$ is stable between 700–800°C in a wide field of the system K_3VO_4–$Mg_3(VO_4)_2$–$HoVO_4$ but at the realisation of substitutions by exclusively in a heterovalent scheme $K^+ + Ho^{3+} \Rightarrow 2Mg^{2+}$, similar to the formation of micas. This compound has a narrow homogeneity area with K^+ and Ho^{3+} simultaneously substituting for Mg^{2+} with a maximum magnesium content up to the composition $K_{2.85}Mg_{0.3}Ho_{0.85}(VO_4)_2$ (Table 1). This coexists either with $HoVO_4$ or with K_3VO_4. In this case, as with $K_3Y(VO_4)_2$, solid solution formation with the structure of α-K_3VO_4 seems to be possible.

Magnesium orthovanadate exists within three-phase fields of the ternary system also.

At higher contents of $Mg_3(VO_4)_2$, the binary compound $K_3Ho(VO_4)_2$ becomes unstable and holmium vanadate, $HoVO_4$, crystallises in a wide range of initial compositions. No ternary vanadates containing simultaneously potassium, magnesium and holmium were shown to be formed. In the sample of composition $KMgHo(VO_4)_2$ (point 10 Fig. 1) there is only the Ho bearing phase $HoVO_4$.

In contrast to magnesium introductions, any attempt to introduce calcium and strontium into K and Ho sites of this network, in accordance with the above schemes, leads to the formation of solid solutions. Those contain Ca and Sr within the limits corresponding to the composition $K_{2.9}(Ca,Sr)_{0.2}(VO_4)_2$. No substitutions have been observed in the case of barium.

Thus, a narrow range of homogeneity of $K_3Ho(VO_4)_2$ in the ternary system after introducing alkaline earths was achieved exclusively with magnesium. No similar solid solutions are formed when calcium, strontium and barium substitutions are attempted. It may be an indirect but reliable indication as to the character of magnesium sites in the glazerite-like structure. Actually, size considerations permit the suggestion that magnesium preferably locates within the oxygen octahedral environment, e.g. in the holmium positions. The larger ionic radii of Ca, Sr and Ba alter the conditions of stability of oxygen octahedra. So, the Δr value for the K–Mg couple is 0.62 Å, fitting better to the stability criteria of glazerite network than for the pairs K–Ca, K–Sr and K–Ba, where these values are substantially lower than 0.62 Å, being equal to 0.38; 0.20 and 0.03 Å, respectively.

Partial substitutions $K^{+}+Ho^{3+} \Rightarrow 2Mg^{2}$ in the binary vanadate of potassium–holmium open the possibilities for the synthesis of vanadates with gradually changing physical characteristics, for example, obtaining desired relative values of electronic and ionic components of electrical conductivity.

So the compound $K_3Ho(VO_4)_2$ retains glazerite-like structure after its doping with small quantities of magnesium according to the heterovalent substitution scheme. In the quasiternary system K_3VO_4–$Mg_3(VO_4)_2$–$HoVO_4$ the homogeneity region $K_{3-x}Mg_{2x}Ho_{1-x}(VO_4)_2$ is narrow ($x=0.15$) at 700–800°C.

Binary vanadate $K_3Ho(VO_4)_2$ doped with magnesium is stable up to the concentration 25 mol.% of $Mg_3(VO_4)_2$. As the $Mg_3(VO_4)_2$ amount increases the binary vanadate is destroyed, forming $HoVO_4$. The discrete compound '$KMHo(VO_4)_2$' like the ternary sodium vanadates $NaMLa(VO_4)_2$ (M=Ca,Sr,Ba) [7,8] does not form.

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