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Thermodynamic modeling, structural and spectroscopic studies of the $KNbWO_6$–$KSbWO_6$–$KTaWO_6$ system

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ABSTRACT

In the present work some structural and thermodynamic features in $KNb_xSb_yTa_zWO_6$ solid-state solutions were investigated. A mathematical subregular ternary solutions model is advanced. The compounds have been structurally studied using X-ray diffraction. In particular, structure of individual compounds ($KNbWO_6$, $KSbWO_6$ and $KTaWO_6$) was refined by the Rietveld method (space group $Fd3m$, $Z=8$). IR and Raman spectroscopies were used to assign vibrational bands and determine structural pecularities. The differential scanning calorimetry was applied to measure decomposition temperature of compounds under study and to detect any possible phase transitions.

1. Introduction

Pyrochlore is important in nature as an ore mineral (Nb and Ta) and as a carrier of lanthanide and actinide (Th and U) elements in the Earth's crust. The structure type exhibits a range of useful properties for materials science applications including ionic conductivity (both cations and anions) [1,2], electrical conductivity, magnetic [3–6] and ferroelectric [7] properties. Besides materials on basis of KA^VWO_6 (A^V – Nb, Sb, Ta) compounds can be used as catalysts due to content of transition metals.

The object of our investigation is complex oxides containing potassium, tungsten and transition metals with oxidation number +5 and solid-state solution on their base. Despite the extensive interest in defect pyrochlore oxides, thermodynamic and physicochemical data are presented in bare number of publications. Therefore detailed investigations of these compounds are especially important.

The goals of this work include detailed structural, spectroscopic and thermal stability studies of individual phases (KA^VWO_6 (A^V – Nb, Sb, Ta)), as well as thermodynamic modeling of the $KNb_xSb_yTa_zWO_6$ system.

2. Experimental

2.1. Samples

$KNb_xSb_yTa_zWO_6$ solid solution was prepared by the solid-state reaction between WO_3, Nb_2O_5, Sb_2O_3, Ta_2O_5 and KNO_3. The synthesis was performed in a porcelain crucible, into which the reaction mixture with the corresponding atomic ratio $1K+1W+xNb+ySb+zTa$ was loaded. In order to find out the mixing temperatures, the process was realized in several stages with temperature rise of 25 K and holding the reaction mixture at every temperature during 50 h. This process was started at 973 K. The choice of initial temperature is determined by the purity of studied compounds with pyrochlore structure compared to additive products, which form at lower temperature. The phase individuality of the compounds was verified after every synthesis step by X-ray diffraction. The X-ray data and estimated impurity content (0.5–1 wt%) in the substances allowed us to conclude that every of the studied samples was composed of an individual crystalline compound. To prove the atomic ration $1K+1W+xNb+ySb+zTa$ the obtained samples were analyzed on a Shimadzu energy-dispersive roentgen fluorescent spectrometer EDX-900HS (from $_{11}Na$ to $_{92}U$) with sensitive detector without liquid nitrogen.

In the case when at a given temperature a sample was detected to be two-phase, i.e. its X-ray diffraction pattern was a superposition of X-ray diffraction patterns of two solid solutions, the temperature was further increased by 25 K. Thus we took value

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Table 1
Structural parameters, experimental and theoretical miscibility data for the isovalent substitutional solid solution of composition $KNb_xSb_yTa_zWO_6$ (all data presented at $T = 298$ K).

x	y	z	a (Å)	$\Delta_{mix}V$ (Å^3)	T_{mix} (K)	$\Delta_{mix}H^\circ$ (calc.) (kJ/mol)	$\Delta_{mix}H$ (model.) (kJ/mol)	$\Delta\bar{H}_1$ (kJ/mol)	$\Delta\bar{H}_2$ (kJ/mol)	$\Delta\bar{H}_3$ (kJ/mol)	$\ln\gamma_1$	$\ln\gamma_2$	$\ln\gamma_3$
1	0	0	10.5001(1)	0	–	0	0	0	22.20	22.20	0	8.96	8.96
0	1	0	10.23671(7)	0	–	0	0	31.08	0	22.20	12.54	0	8.96
0	0	1	10.4695(1)	0	–	0	0	11.10	31.08	0	4.48	12.54	0
0.125	0.875	0	10.2365(7)	−10.6	1073	3.36	3.28	22.10	0.59	31.28	8.91	0.24	12.62
0.25	0.75	0	10.2651(14)	−12.4	1098	5.13	5.41	14.99	2.22	33.75	6.05	0.90	13.62
0.375	0.625	0	10.2934(9)	−14.0	1123	6.18	6.50	9.54	4.68	31.63	3.85	1.89	12.77
0.5	0.5	0	10.3627(34)	−2.4	1123	6.47	6.66	5.55	7.77	26.92	2.24	3.13	10.86
0.625	0.375	0	10.4255(5)	7.3	1098	6.04	5.98	2.81	11.27	21.61	1.13	4.55	8.72
0.75	0.25	0	10.4589(5)	7.7	1073	5.02	4.58	1.11	14.99	17.73	0.45	6.05	7.15
0.875	0.125	0	10.4768(16)	2.9	1023	3.20	2.55	0.24	18.70	17.25	0.10	7.54	6.96
0.125	0	0.875	10.4598(17)	−4.4	–	*1.76*	1.37	10.62	40.20	0.04	4.29	16.22	0.02
0.25	0	0.75	10.4659(9)	−3.7	–	*2.91*	2.60	9.37	41.87	0.35	3.78	16.89	0.14
0.375	0	0.625	10.4947(10)	4.5	–	*3.63*	3.58	7.59	38.35	1.17	3.06	15.47	0.47
0.5	0	0.5	10.4914(8)	2.2	–	*3.88*	4.16	5.55	31.91	2.78	2.24	12.87	1.12
0.625	0	0.375	10.4923(7)	1.2	–	*3.63*	4.23	3.51	24.81	5.42	1.42	10.01	2.19
0.75	0	0.25	10.4998(11)	2.5	–	*2.91*	3.64	1.73	19.32	9.37	0.70	7.79	3.78
0.875	0	0.125	10.4747(32)	−7.1	–	*1.76*	2.28	0.48	17.69	14.87	0.19	7.14	6.00
0	0.125	0.875	10.4553(28)	4.7	1023	3.20	3.28	23.80	22.10	0.59	9.60	8.91	0.24
0	0.25	0.75	10.4324(8)	6.6	1098	5.13	5.41	34.41	14.99	2.22	13.88	6.05	0.90
0	0.375	0.625	10.4154(6)	10.4	1148	6.31	6.50	42.53	9.54	4.68	17.16	3.85	1.89
0	0.5	0.5	10.3602(9)	1.9	1173	6.76	6.66	47.73	5.55	7.77	19.26	2.24	3.14
0	0.625	0.375	10.2650(24)	−19.2	1173	6.45	5.98	49.60	2.81	11.27	20.01	1.13	4.55
0	0.75	0.25	10.2559(14)	−12.7	1123	5.25	4.58	47.73	1.11	14.99	19.26	0.45	6.05
0	0.875	0.125	10.2116(33)	−17.3	1048	3.28	2.55	41.69	0.24	18.70	16.82	0.10	7.55
0.5	0.25	0.25	10.4512(14)	7.6	1073	9.28	8.43	1.08	18.28	13.29	0.43	7.37	5.36
0.25	0.5	0.25	10.3452(20)	−5.5	1198	10.36	10.49	11.43	7.23	16.08	4.61	2.92	6.49
0.25	0.25	0.5	10.4517(15)	10.3	1098	9.49	9.70	8.86	20.31	4.80	3.58	8.19	1.94
0.333	0.333	0.333	10.4260(13)	8.4	1123	10.26	10.44	5.02	15.21	11.10	2.02	6.14	4.48

Data obtained by extrapolation of experimental data was signed by italic type.

of minimal temperature, i.e. the temperature at which the sample was found out to be monophasic, as the mixing temperature (see Table 1).

In order to decrease the kinetic factor connected in general with diffusion processes, in every synthesis step the samples were dispersed using the vibration grinding mill Mixer/Mill5100. This treatment led to increase of the surface area of interacting particles. Then the powders were pressed at 100 bar. After determining the mixing temperatures the samples were calcined at 1273 K to increase their crystallinity.

As can be seen in Table 1 the mixing temperatures for $KNbWO_6$–$KTaWO_6$ system are not defined since their values are lower than synthesis temperatures of these solid solutions. Therefore, formation of monophase sample was observed already at 973 K. It is worth to notice that the obtained solid solutions are stabilized with respect to unmixing process at room temperature.

2.2. Apparatus and measurement procedure

For structural investigations, X-ray diffraction patterns of all samples were recorded on a Shimadzu X-ray diffractometer XRD-6000 (Cu Kα radiation, geometry θ–2θ) in the 2θ range from 10° to 120° with scan increment of 0.02°. Rietveld analysis and structure refinement [8] were carried out using RIETAN-94 software [9].

Polycrystalline infrared spectra were measured with a Biorad 575C FT-IR spectrometer in KBr suspension for the 1000–400 cm^{-1} region and in Nujol suspension for the 500–40 cm^{-1} region. FT-Raman spectra were measured using BRUKER 110/S spectrometer. Excitation was performed with a 1064 nm line of a YAG:Nd^{3+} laser. Both IR and Raman spectra were recorded with a spectral resolution of 2 cm^{-1}.

Thermal behavior was carried out with DSC Labsys from Setaram in a platinum crucible ranging from 293 to 1173 K (heating rate 0.167 K/s).

3. Results and discussion

3.1. Crystal structure

Structure of individual compounds ($KNbWO_6$, $KSbWO_6$ and $KTaWO_6$) was refined by the Rietveld method, assuming space group $Fd\bar{3}m$ and having defect pyrochlore structure. The initial model included the atomic coordinates in the structure of $RbNbWO_6$ [10]. The details of the X-ray diffraction experiment and structure refinement data are listed in Table 2. Fig. 1 represents the measured, simulated, and difference X-ray diffraction patterns for $KNbWO_6$, as well as a pattern of lines corresponding to reflection maxima. There is a good agreement between the measured and simulated patterns. Table 3 lists the coordinates of the atoms and their isotropic thermal parameters. The refined model yielded positive isotropic thermal parameters B for all atoms. Table 4 lists the interatomic distances and valence angles in the structure and Fig. 2

Table 2
Details of the X-ray diffraction experiment and the results of the structure refinement for KA^VWO_6 (A^V – Nb, Sb, Ta) (all data presented at $T = 298$ K).

	$KNbWO_6$	$KSbWO_6$	$KTaWO_6$
Space group	$Fd\bar{3}m$		
Z	8		
2θ range (°)	10–120		
a (Å)	10.5001(1)	10.23671(7)	10.4695(1)
V (Å^3)	1157.67(2)	1072.71(1)	1147.57(3)
d (kg m^{-3})	4752.9	5488.6	5819.7
'Number of reflections	59	63	55
Number of refined parameters	25	27	27
Structural parameters	4	6	4
Others	21	21	23
R_{wp}; R_p (%)	8.53; 5.40	3.75; 2.63	10.11; 6.48

Definition of reliability factors R_{wp} and R_p are given as follows: $R_{wp} = \{(\sum w_i[y_{iobs} - y_{icalc}]^2/(\sum w_i[y_{iobs}]^2)\}^{1/2}$; $R_p = (\sum |y_{iobs} - y_{icalc}|)/(\sum y_{iobs})$.