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Synthesis, crystal structure and vibrational spectra of $KCrV_2O_7$ and $RbCrV_2O_7$

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Abstract

$KCrV_2O_7$ and $RbCrV_2O_7$ have been synthesized and their crystal structures have been determined using X-ray and neutron powder diffraction techniques. The phases crystallizes in space group $P2/c$ with unit cell parameters for $KCrV_2O_7$: $a = 7.9526(1)$ Å, $b = 4.87543(5)$ Å, $c = 6.8910(1)$ Å and $\beta = 101.162(1)°$ and $RbCrV_2O_7$: $a = 8.2361(1)$ Å, $b = 4.89480(4)$ Å, $c = 6.8980(1)$ Å and $\beta = 100.893(1)°$. The unit cell was confirmed by selected area electron diffraction studies. The crystal structure consists of two-dimensional $CrV_2O_7^-$ slabs parallel to the (100)-plane, formed from zigzag chains of face- and edge-sharing VO_6 octahedra connected through CrO_6-octahedra. The VO_6 octahedra are very distorted including a short VO-vanadyl unit. The alkaline metal ions placed in the inter-slab space have coordination number $10 + 2$ forming distorted triangular orthobicupolas. The infrared and Raman spectra of the compounds are presented and discussed.

Keywords: Oxovanadates; Crystal structure; Raman spectra; IR-spectra; Solid state chemistry; Electron diffraction; Powder diffraction

1. Introduction

There are rather few reports on the crystal chemistry of complex oxides in the system A_2O–Cr_2O_3–V_2O_5 (A—alkali metal). Only $Li_3CrV_2O_8$ (space group $Fd\bar{3}m$, $Z = 4$) and $Na_3Cr_2V_3O_{12}$ (space group $Ia\bar{3}d$, $Z = 8$), with structures related to spinel and garnet, respectively, have been studied in detail although no refined atomic coordinates are available [1,2]. $NaCrV_2O_7$ [3] and $KCrV_2O_7$ [4] have been reported as well, although not their structures. In this report we present the synthesis and crystal structure determination using X-ray and neutron powder diffraction and transmission electron microscopy, as well as an infrared and Raman study of the vibrational spectra of $KCrV_2O_7$ and $RbCrV_2O_7$.

2. Experimental

$KCrV_2O_7$ and $RbCrV_2O_7$ were prepared by solid-state reaction in air using stoichiometric mixtures of $A_2Cr_2O_7$ (99.9%) (A = K, Rb) and V_2O_5 (99.99%) according to the formula:

$$2A_2Cr_2O_7 + 4V_2O_5 \rightarrow 4ACrV_2O_7 + 3O_2\uparrow.$$

The mixtures were placed in platinum crucibles and annealed at a temperature that was increased from 350 to 600 °C in steps of 50 °C with hold time 4 h with intermediate cooling down and regrinding in agate mortar.

All the XRD patterns were collected at room temperature on a transmission STADI-P diffractometer (STOE, Germany) equipped with a linear mini-PSD detector, using Cu K_{α_1} radiation in the 2θ range 2° to 120° with a step of 0.02°. Polycrystalline silicon ($a = 5.43075(5)$ Å) was used as external standard. The phase purity of the products from the synthesis was checked in an optical microscope (polarized light) and by comparing their X-ray powder diffraction patterns (XRD) with those in the PDF2 database (powder diffraction file, ICDD, USA) released 2004.

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Neutron powder diffraction data for $KCrV_2O_7$ and $RbCrV_2O_7$ were collected at room temperature with the NPD and the R2D2 diffractometers at the Swedish research reactor at NFL, Studsvik, respectively. A thin vanadium can with diameter 6 mm was used as sample holder. Both NPD and R2D2 were equipped with ^{3}He detectors containing 10′ Gd coated mylar collimators, although, the former had a Cu(220) and the latter a Ge(511) monochromator. The neutron wave-lengths were 1.47 Å (NPD) for $KCrV_2O_7$ and 1.55 Å (R2D2) for $RbCrV_2O_7$.

The crystal structure was determined basing on X-ray data with the program EXPO [5] and the final refinements were carried out with the GSAS program suite [6]. The latter software allows the simultaneous use of X-ray and neutron data in the refinements. When combining XRD and neutron data in a refinement one has to remember that photons are scattered by electrons and neutrons, in this case by the nucleus of the atoms. The result of individual refinements will therefore not completely coincide. However, both XRD and neutron powder diffraction data have their weakness. For light elements like oxygen the low scattering power compared to rubidium and vanadium can be a problem while for neutron the close to zero cross section for vanadium is a limitation. We therefore decided to use one model for both data sets. The unit cell parameters were refined using the XRD data. These values were then used for the neutron data and the wavelength was refined instead.

The experimental densities of the XRD-monophasic samples were determined by pycnometric (bottle method) measurements in CCl_4.

For the transmission electron microscopy studies (SAED—selected area electron diffraction, HREM—high resolution electron microscopy, EDS—energy-dispersed X-ray microanalysis), the samples were crushed in n-butanol. A drop of this dispersion was put on a copper grid covered with a holey carbon film. The microscope used was a JEOL 2000FX, operated at 200 kV, equipped with a LINK AN10000 EDX system and JEOL 3010 operated at 300 kV.

The Raman spectra were recorded on a Renishaw RM-1000 laser Raman microscope system at ambient temperature with excitation wavelength $\lambda = 514.5$ nm (Ar^+, power of laser ~100 mW). The spectral resolution and the accuracy in the Raman shift are both estimated to be about 1 cm^{-1}. The IR spectra were recorded as vaseline oil mulls with a "Spectrum-one" (Perkin Elmer) spectrometer in the wave-number region 400–1200 cm^{-1}. The resolution was about 0.5 cm^{-1} in the investigated spectral range.

3. Results

After the synthesis, deep brown XRD single-phase samples were obtained of both the potassium and rubidium compound. All reflections in the corresponding XRD pattern records could be indexed with monoclinic unit cells, Table 1. An analysis of systematically absent reflections in XRD and electron diffraction patterns ($h0l$: $l = 2n$; $00l$: $l = 2n$) indicates a primitive lattice and two possible space groups: Pc and $P2/c$. Selected area diffraction patterns of $KCrV_2O_7$ and $RbCrV_2O_7$ viewed along the main zone axes are shown in Figs. 1 and 2. The weak streaking along the reciprocal a-axes in the zone axes patterns is caused by the two dimensional character of the structure leading to small crystallite sizes in that direction and not disorder. The well-ordered character of the crystal structure is seen in the HREM image of the $RbCrV_2O_7$ shown in Fig. 3. EDS analyses of $KCrV_2O_7$ and $RbCrV_2O_7$ were made to check the purity of the samples. The obtained compositions were in agreement with the nominal composition. However, some crystallites with

Table 1
Crystal data for $KCrV_2O_7$ and $RbCrV_2O_7$

	$KCrV_2O_7$	$RbCrV_2O_7$
Unit cell parameters (Å)[a]	$a = 7.9526(1)$	$a = 8.2361(1)$
	$b = 4.87543(5)$	$b = 4.89480(4)$
	$c = 6.8910(1)$	$c = 6.8980(1)$
	$\beta = 101.162(1)°$	$\beta = 100.893(1)°$
Unit cell volume (Å^3)	262.1(1)	273.1(1)
Space group	$P2/c$	$P2/c$
Formula units, Z	2	2
Number of reflections	423 (598)	440 (526)
Number of parameters	88	88
R_p, R_{wp} (%)	2.70[b] (3.11)[c], 3.40 (3.93)	1.21 (3.02), 1.67 (4.05)
$R(F^2)$ (%)	7.49 (3.54)	8.67 (5.11)
χ^2	1.171	2.701

[a] From X-ray powder diffraction data. [b] Neutron powder diffraction data. [c] X-ray powder diffraction data within ( ).

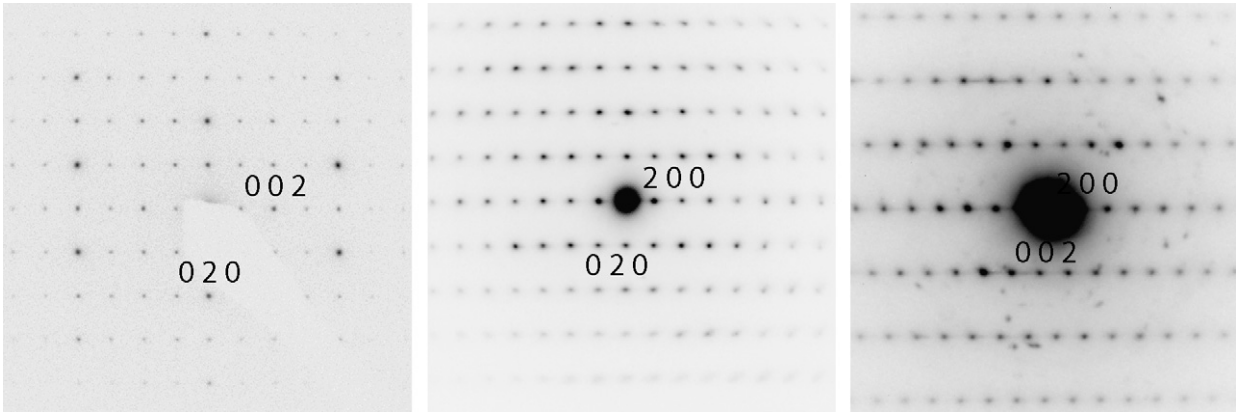

Fig. 1. Selected area electron diffraction pattern of $RbCrV_2O_7$ recorded along [100], [001] and [010].