

X-ray diffraction studies of vanadium oxygen bronzes: $M_xV_2O_5$

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Introduction

The triple metal oxides $nM_2O \cdot mV_2O_4 \cdot pV_2O_5$ ($M = \text{Li, Na, K, Ag or Cu}$) with monoclinic structures exhibit unique physical (electrical, optical, mechanical etc) and chemical (high resistance to acids) properties and are often called "bronzes" due to their similarity to tungsten bronzes [1]. Their applications include electric batteries and selective electrodes in chemistry. The distorted VO_6 octahedra with common edges and corners form a rigid cage with tunnels spread along the monoclinic axis in the structure. The M metals are located in those tunnels. It is generally believed that unusual properties originate from special electronic states of the M and V atoms. These structures are quasi-one-dimensional conductors due to high anisotropy of the electric conductivity in the monoclinic direction. Such anisotropy can be explained by the existence of the $V^{4+}-V^{4+}$ spin-singlet pairs (bipolarons) formed by strong electron-phonon coupling [2] which travel along the monoclinic axis. The conductivity in the other directions is due to diffusive electron hopping motion. The polaron condensation and ordering phenomena were observed by NMR and X-ray diffuse scattering, and some satellite reflections were detected in several alkali bronze β -phases [3] possibly due to the bipolaron ordering. The aim of this study is to re-examine the crystal structure and the electron density in several $M_xV_2O_5$ in attempt to improve our understanding of the chemical bonding in these compounds.

Experimental

Synchrotron X-ray diffraction data sets for $\beta\text{-Na}_xV_2O_5$ ($x=0.28$), $\text{Ag}_xV_2O_5$ ($x=0.33$) and $\beta'\text{-Cu}_xV_2O_5$ ($x=0.65$) were collected over complete spheres up to $(\sin\theta/\lambda)_{\max}=1.1 \text{ \AA}^{-1}$ at room temperatures with $\lambda=0.7 \text{ \AA}$ radiation using the BL14A beam line four-circle diffractometer. In order to reduce absorption and extinction effects, a tiny, naturally faced specimen with dimensions less than $50 \mu\text{m}$ was used. Analytical absorption, Lorentz and polarization corrections and anomalous dispersion were applied. Symmetrically equivalent reflections were averaged. Independent structural parameters, including the scale factor, positional and thermal displacement parameters for all atoms were refined by conventional full-matrix least squares. Charge density multipole refinements were performed for $\beta\text{-Na}_{0.28}V_2O_5$ and $\beta'\text{-Cu}_{0.65}V_2O_5$ structures so far.

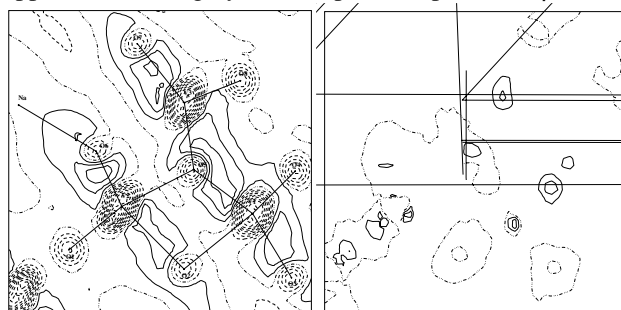
Results and discussion

The Na isomorph is the most studied β -phase. The three different types of V atoms, the Na atom and the seven different O atoms occupy the 4i (m) crystallographic positions in the unit cell (sp.gr. C2/m). The Na atom

positions are approximately half occupied. The eighth O atom is in 2a (2/m) position with fixed parameters. One of the conductivity models suggests the ordered alternation of the Na sites occupations along the monoclinic axis. This requires the doubling of the b cell parameter. However, no superstructure reflections related to this doubling has been detected for $\beta\text{-Na}_{0.28}V_2O_5$. The second model suggests the random alternation of the Na sites occupations and no changes of the unit cell parameters are required. This model places the Na atoms one under another along the y-axis.

The Cu atoms in $\beta'\text{-Cu}_{0.65}V_2O_5$ (sp. gr. C2/m), contrary to the Na compound, occupy three positions: one Cu1 is in 4(i) position with coordinates $x=0.541$, $y=0$ and $z=0.344$ and two Cu2 atoms in 8(j) position with coordinates $x=0.529$, $y=0.038$ and $z=0.358$ (shifted away from the mirror plane and symmetry related).

Static deformation charge density maps ($\Delta\rho$) in the (010) plane (contours $0.2e/\text{\AA}^3$) for $\beta\text{-Na}_{0.28}V_2O_5$ and $\beta'\text{-Cu}_{0.65}V_2O_5$ in figure below were calculated after multipole refinement. The $\Delta\rho$ map for $\beta\text{-Na}_{0.28}V_2O_5$ is appeared to be highly anisotropic. The positive $\Delta\rho$ (more



covalency) is predominant in the approximate (20 0 1) plane. This reflects the strong bonds between atoms in the plane, whereas there are no such 'covalent' bonds between these planes or sheets. The excess $\Delta\rho$ -density in the V-O bonds forms the extended regions of the positive density along the monoclinic b axis. The atomic charges were estimated from the multipole model, however there is no correlation between the atomic charges and the expected positions for the five- and the four-valence vanadium atoms.

References

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