



Synthesis and Electronic Properties of β -RbNd(MoO₄)₂†

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The electronic structure of β -RbNd(MoO₄)₂ has been evaluated from experimental and theoretical points of view. For the molybdate, X-ray photoelectron valence-band spectra have been measured. The total and partial densities of states of the constituent atoms of β -RbNd(MoO₄)₂ have been calculated using the FP-LAPW method. The FP-LAPW data reveal that main contributors in the valence-band region of β -RbNd(MoO₄)₂ are the Rb 4*p*-, Nd 4*f*-, Mo 4*d*- and O 2*p*-like states.

Keywords: β -RbNd(MoO₄)₂, Electronic structure, *Ab initio* calculations, X-Ray photoelectron spectroscopy.

INTRODUCTION

Metal molybdates have attracted considerable attention for potential applications in photoluminescence, scintillators, photocatalysis hosts for lanthanide-activated lasers and humidity sensors¹⁻⁴. The large family of binary molybdates with the general formula RbLn(MoO₄)₂, where Ln is a rare-earth element, was discovered many years ago^{1,3}. Generally, the RbLn(MoO₄)₂ crystal family shows evident potentials for creation of new laser host and luminescence materials. The existence of two polymorphous modifications, mainly α and β phases, was found for RbNd(MoO₄)₂ with a phase transition¹ occurring at 710 °C. Recently, the crystal structures of the orthorhombic polymorphous modification β -RbLn(MoO₄)₂ (Ln = Nd, Sm) were refined in space group *Pbcn* and spectroscopic properties of the compounds were evaluated^{5,6}. The layered crystal structure of β -RbNd(MoO₄)₂ is shown in Fig. 1 and is related to the KY(MoO₄)₂ type^{7,8}. The present study is aimed at synthesis and complex evaluation of the electronic structure of RbNd(MoO₄)₂ by experimental and theoretical methods.

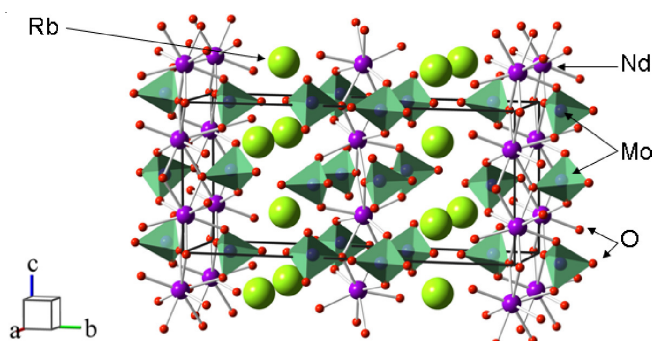


Fig. 1. Crystal structure of β -RbNd(MoO₄)₂, space group *Pbcn*

EXPERIMENTAL

Polycrystalline β -RbNd(MoO₄)₂ was derived by solid state synthesis using a stoichiometric ratio mixture of analytically pure MoO₃ (99.9 %), Rb₂CO₃ (99.99 %) and Nd₂O₃ (> 99.9 %) as starting materials. Initially, rubidium and neodymium molybdates were prepared by routine ceramic technique. Then, the powder mixture of these compounds was preheated at T = 723 K for 50 h and was annealed at T = 873 K for 150 h to

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yield the RbNd(MoO₄)₂ composition. To minimize the MoO₃ loss at high temperatures, the multistage method with step-by-step temperature increase is optimal for synthesis⁹⁻¹². Final product of the high temperature synthesis was found to be of light-purple colour that is common for Nd³⁺-containing oxides. The XRD measurements were produced by an D8 Advance Bruker AXS device employing CuK_α radiation.

XPS valence-band and core-level spectra of RbNd(MoO₄)₂ were measured using the UHV-Analysis-System assembled by SPECS Surface Nano Analysis Company (Berlin, Germany). The system is equipped with a PHOIBOS 150 hemispherical analyzer. Energy drift due to charging effects was calibrated, taking the XPS C 1s (284.6 eV) core-level spectrum of hydrocarbons as it was suggested for tungstate materials¹³⁻¹⁵. On the basis of density functional theory (DFT), our *ab initio* band-structure calculations of RbNd(MoO₄)₂ are performed using the full potential linearized augmented plane wave (FP-LAPW) method with the WIEN97 code¹⁶.

RESULTS AND DISCUSSION

The final powder product was formed by slightly agglomerated plate-like microcrystals with typical dimensions 12 μm × 6 μm × 1 μm and smoothed edges. Crystal habit is appeared to be governed by a layered structure typical for MLn(MoO₄)₂-type molybdates^{5,6}. The XRD pattern recorded from the powder confirms the presence of pure β -RbNd(MoO₄)₂ phase⁵. XPS spectrum showed that all the spectral features, except of the carbon 1s level at 284.6 eV originated from adventitious hydrocarbons adsorbed on the surface, can be attributed to the constituent element core-levels or Auger lines. It should be mentioned that the relative intensity of the C 1s core-level line for the surface of β -RbNd(MoO₄)₂ sample was found to be rather weak. The relative element contents were estimated using the detailed spectra of the XPS Rb 3d, Nd 3d_{5/2}, Mo 3d_{5/2} and O 1s core-level lines and the tabulated data on corresponding atomic sensitivity factors (ASF)¹⁷. The resulting composition Rb:Nd:Mo:O = 0.075:0.069:0.188:0.668 is in good agreement with the nominal composition Rb:Nd:Mo:O = 0.08:0.08:0.17:0.67 of β -RbNd(MoO₄)₂.

A number of element core levels are found at low BE values as it is shown in Fig. 2, where the XPS valence-band (VB) spectrum (including upper Nd 5s, Mo 4p, Rb 4s, Nd 5p, O 2s and Rb 4b core-levels) recorded for β -RbNd(MoO₄)₂ is presented¹⁸⁻²². From the figure, it is obvious that two fine-structure peculiarities, namely A and B, are well resolved on the XPS valence-band spectrum of β -RbNd(MoO₄)₂, where the mixed valence states are located (at BE < 10 eV). In the theoretical calculations of β -RbNd(MoO₄)₂ the total and partial densities of states were calculated (Fig. 3). The comparison shows that the main contributors in the valence-band region of RbNd(MoO₄)₂ are the Rb 4p-, Nd 4f-, Mo 4d- and O 2p-like states. The contributions of the Nd 4f-like states dominate at the top of the valence band, the O 2p-like states contribute mainly into the upper portion of the valence band with also significant contributions throughout the whole valence-band region, whilst the Mo 4d-like states contribute mainly into the lower portion the valence band of the molybdate studied. With respect to the occupation of the electronic states associated

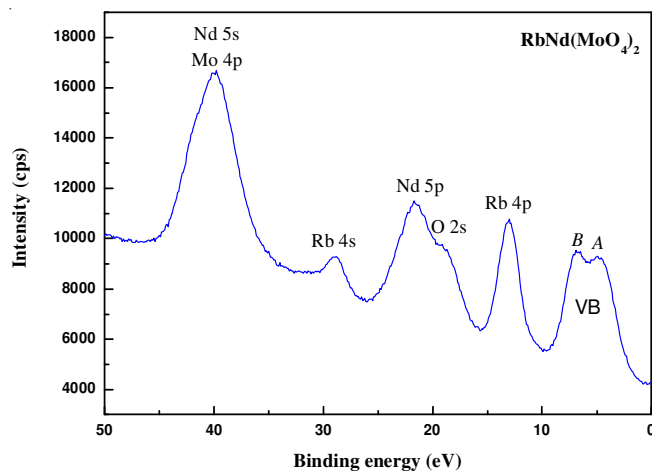


Fig. 2. XPS valence-band (VB) spectrum of the β -RbNd(MoO₄)₂

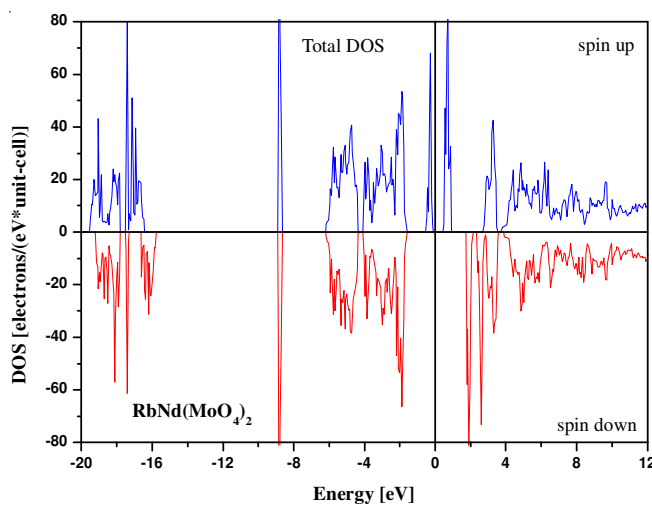


Fig. 3. Plot of the total densities of states of β -RbNd(MoO₄)₂

with molybdenum and oxygen atoms in the valence-band region of RbNd(MoO₄)₂, the theoretical FP-LAPW data are confirmed experimentally by comparison on a common energy scale of the X-ray photoelectron spectrum in the molybdate under consideration.

From the structural point of view, the wide substitution by Ln elements is possible in β -RbNd(MoO₄)₂ lattice at Nd positions. It should be pointed that complex doping by Ln elements is widely used for the creation of effective luminescent materials. As it was shown by present analysis, the Nd-related states are at the top of the valence band in β -RbNd(MoO₄)₂ and the Ln-doping may induce drastic variation of the band structure²³⁻²⁶.

Conclusion

The β -RbNd(MoO₄)₂ sample is prepared with solid state synthesis and valence band is measured by XPS. The FP-LAPW calculations reveal that the valence band of the RbNd(MoO₄)₂ molybdate is dominated by contributors of the Rb 4p-, Nd 4f-, Mo 4d- and O 2p-like states. In particular, the O 2p- and Mo 4d-like states contribute mainly into the upper and lower portions of the valence band, respectively. The calculated band structure is in good relation with XPS measurements.

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