

MS15-P13 Structural peculiarities and structure-optical property relationships of doped ($\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6\text{:Cr/Ni}$ and $\text{SrMoO}_4\text{:Tm/Ho}$ crystals

Galina M. Kuzmicheva¹, Irina A. Kurova¹, Lyudmila I. Ivleva², Victor B. Rybakov³, A. Cousson⁴

1. Moscow Technological University, MITHT
2. Prokhorov General Physics Institute, Russian Academy Sciences
3. Lomonosov State University
4. Laboratoire Leon Brillouin, CEA Saclay

email: galina_kuzmicheva@list.ru

Doping is one of the main ways to entrance properties of crystals. The aim of paper is to establish the role of doping of single crystals with initial compositions $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ (sp.gr. P4bm) (SBN), grown by Czochralski, and SrMoO_4 (sp.gr. I4/a) (SMO), grown by Stepanov, by Cr^{3+} and Ni^{3+} , and Tm^{3+} and Ho^{3+} ions, respectively.

The neutron diffraction analysis of SBN ($\sim 5 \times 5 \times 5 \text{ mm}^3$) was carried out on diffractometer 5C2 (LLB, France; $\lambda = 0.83 \text{ \AA}$). The refined compositions of SBN were found to be different from the initial charge compositions, wherein the doping enhances such differences. Analysis of cation-anion internuclear distances together with calculation of bond-valence sums showed that Nb1 and Nb2 are located in distorted octahedra with split vertices, forming a framework with three types of channels: Sr1 atoms are located in cuboctahedra (square channels), Ba2 and Sr2 atoms are located in distorted three-capped trigonal prisms and five-capped pentagonal prisms, respectively, with split vertices in base planes (pentagonal channels). Displacement of electron density in Nb1 and Sr2 polyhedra, responsible for covalent bond and second-order nonlinear susceptibility, has been revealed. It was found that Cr^{3+} ions occupy triangular cavities with distorted octahedral coordination and Ni ions are located in distorted semi-octahedra near Nb2 and Nb1 sites. It leads to appearance of additional energy levels, which enhances photo-refractive properties and results in shift of the absorption edge to longer wavelengths.

The X-ray diffraction analysis of SMO crystals ($\sim 0.1 \times 0.1 \times 0.1 \text{ mm}^3$) was carried out on CAD-4 diffractometer (MoK α , graphite monochromator). Introduction of dopants into the melt in the form of $\text{RE}^{3+}\text{Nb}_2\text{O}_6$ ($\text{RE}^{3+} = \text{Tm}, \text{Ho}$) with distorted scheelite structure (that is favorable for isomorphic substitution and maintenance of electrical neutrality leads to different behavior of RE^{3+} in SMO structure: to partial substitution of Sr^{2+} (in dodecahedra) and Mo^{6+} (in tetrahedra) ions by Ho^{3+} and Nb^{5+} ions near Sr^{2+} and Mo^{6+} defect sites. Spectroscopic investigations of SMO:Tm have shown that the maximum absorption cross section of Tm^{3+} lies at 795 nm and reaches $1.1 \cdot 10^{-20} \text{ cm}^2$ for π -polarized radiation, higher than that in $\text{Y}_3\text{Al}_5\text{O}_{12}$ and LiYF_3 crystals.

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Keywords: barium strontium niobate, scheelite, diffraction study, optical properties

MS15-P14 Structural and physicochemical characterization of Basic Calcium Carbonate (BCC)

Christian L. Lengauer¹, Manuel Ripken¹, Florian Gallien², Thomas Schlotterbach²

1. Department of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria
2. Omya GmbH, Gersheimstrasse 1-2, 9722 Gummern, Austria

email: christian.lengauer@univie.ac.at

This study reports investigations on physicochemical characterization, environmental stability and structural features of calcium carbonate hydroxide hydrate, labeled in literature [1,2] as basic calcium carbonate (BCC). Despite the fact of the relevance of BCC in calcium carbonate processing, structural knowledge of this metastable phase is still missing. Therefore, material, precipitated according to the synthesis route described later, was analyzed by means of powder X-ray diffraction (pXRD), thermal analyses (TA), chemical analyses, electron microscopic imaging (SEM) and spectroscopic methods.

The best conditions for the storage of calcium carbonate hydroxide hydrate (basic calcium carbonate - BCC) are in a bone dry non-heated environment. This is confirmed by powder X-ray (pXRD) analysis. Under humid conditions sample material transforms into vaterite-type calcium carbonate, while under a dry heating process it dehydrates and dehydrolyzes to calcite-type calcium carbonate. Under ambient humidity and temperature conditions the dehydrated modification does not convert back to BCC, but also transforms to the vaterite-type calcium carbonate. High quality scanning electron microscopy (SEM) images of a rapidly converted vaterite-type calcium carbonate reveal imperfect pseudomorphs of vaterite after the platy BCC.

According to the observed and calculated weight losses of BCC and data from literature, one can state a mismatch with the prior reported chemical formula, which would require an overall weight loss of -14.9 wt% for $(\text{OH})_2 + 1.5\text{H}_2\text{O}$. As the observed weight loss is here proven to be -12.3 wt%, which is very close to the calculated value for a monohydrate (-12.2 wt%), one can give the corrected chemical formula as $\text{Ca}_3(\text{CO}_3)_2(\text{OH})_2\text{H}_2\text{O}$ for BCC.

Crystallographic analysis reveals the hitherto unknown structure of BCC determined by analyzing pXRD patterns. BCC crystallizes to a monoclinic lattice with space group P_c. The cell parameters of the pseudo-orthorhombic cell are $a = 8.661(1) \text{ \AA}$, $b = 6.557(1) \text{ \AA}$, $c = 7.078(1) \text{ \AA}$, $\beta = 90.08(1)^\circ$ and $V = 401.97(4) \text{ \AA}^3$. The structure model shows similarities with those of portlandite, vaterite and hydromagnesite.

[1] Schimmel G. (1970) Naturwissenschaften, Jg. 57, 38-39.

[2] Matsushita et al. (1993) J. Ceramic Soc. Japan, 101, 895-899.

Keywords: BCC, calcium carbonate hydroxide hydrate