

# **Phase equilibria in the subsolidus region of CaO–Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> ternary oxide system and physicochemical properties of the phases**

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## **ABSTRACT**

The aim of the doctoral thesis was to determine previously unknown phase equilibria in CaO–Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> ternary oxide system in the subsolidus region and to identify and characterize the phases formed in this system. The literature review showed that niobium(V) oxide, one of the compounds constituting the ternary system, exhibits a complex polymorphism and its structural and physicochemical properties, despite many studies, have not been clearly defined. Also, the phase equilibria in the pseudobinary systems constituting CaO–Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> ternary system, i.e. CaO–Nd<sub>2</sub>O<sub>3</sub>, CaO–Nb<sub>2</sub>O<sub>5</sub> and Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> have not been well understood despite many years of research on calcium niobates, neodymium niobates, and double niobates containing calcium and lanthanide, including neodymium.

The results presented in this monograph were obtained mainly by XRD, SEM-EDS, DTA-TGA, IR, Raman, luminescence spectroscopy, UV-Vis-DR and EPR methods. Structural, thermal, optical and electrical properties as well as the morphology of selected phases were characterized. The most important results obtained as part of the doctoral dissertation include:

- Determination of the structural and thermal characteristics of three commercially available powders of Nb<sub>2</sub>O<sub>5</sub>. The research has shown that the crystal structure of the niobium(V) oxide depends on the origin, and thus on the production method, which is not normally disclosed by the manufacturers. It was found that among the tested powders only one was phase pure, the others were a mixture of at least two polymorphs of niobium(V) oxide. The phase equilibria were investigated with the use of Sigma Aldrich niobium(V) oxide, because it is the only one delivered as a pure-phase powder. It is characterized by the highest purity and enables the synthesis of pure-phase calcium niobates.

- Verification and determination of previously unknown phase equilibria in the CaO–Nb<sub>2</sub>O<sub>5</sub> and Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> pseudobinary systems in the entire range of compositions. Structural parameters of single-phase complex oxides were refined using the Rietveld method.
- Determination of the phase equilibria occurring in the Ca<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub>–Nd<sub>2</sub>O<sub>3</sub> and Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>–Nd<sub>3</sub>NbO<sub>7</sub> binary systems, constituting binary cross-sections in the CaO–Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> ternary system. Studies in the subsolidus region have shown the formation of limited solid solutions; the composition limits of their existence were determined and general formulas were defined as: (Ca<sub>4</sub>Nb<sub>2</sub>)<sub>1-x</sub>Nd<sub>2x</sub>O<sub>9-6x</sub> (0 < x < 0,5) and (Ca<sub>2</sub>Nb<sub>2</sub>)<sub>2x</sub>Nd<sub>3</sub>NbO<sub>14x+7</sub> (0 < x < 1). It was shown that (Ca<sub>4</sub>Nb<sub>2</sub>)<sub>1-x</sub>Nd<sub>2x</sub>O<sub>9-6x</sub> (0 < x < 0,5) solid solution crystallizes in monoclinic system with *P21/c* space group related to the high-temperature modification of the Ca<sub>4</sub>Nb<sub>2</sub>O<sub>9</sub> compound. The temperature dependence of magnetic susceptibility and Curie-Weiss temperature of the new solid solution have been also analyzed. The other solid solution, i.e. (Ca<sub>2</sub>Nb<sub>2</sub>)<sub>2x</sub>Nd<sub>3</sub>NbO<sub>14x+7</sub> crystallizes in the orthorhombic structure with the *Pmnc* space group related to the Nd<sub>3</sub>NbO<sub>7</sub> matrix. Based on the IR and Raman spectra, it has been established that two-dimensional layers of the NbO<sub>6</sub> octahedra in the structure of the solid solution are isolated by the layers of the Ca<sup>2+</sup> ions statistically substituted by Nd<sup>3+</sup> ions.
- Statement of crystallographic texturing within the composition limits of both solid solutions, which progresses with an increase in the content of Nd<sup>3+</sup> ions for (Ca<sub>4</sub>Nb<sub>2</sub>)<sub>1-x</sub>Nd<sub>2x</sub>O<sub>9-6x</sub> and with an increase of temperature and Ca<sup>2+</sup> ion content for (Ca<sub>2</sub>Nb<sub>2</sub>)<sub>2x</sub>Nd<sub>3</sub>NbO<sub>14x+7</sub>.
- Spectroscopic studies have shown that the new phases are insulators and have prospective luminescent properties. Substitution of the Nd<sup>3+</sup> ions in the structure of (Ca<sub>2</sub>Nb<sub>2</sub>)<sub>2x</sub>Nd<sub>3</sub>NbO<sub>14x+7</sub> with lanthanum or gadolinium allows to obtain a material with a high luminescence decay time.
- Determination of phase equilibria in the CaO–Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> ternary oxide system at 1200°C in the air atmosphere and elaboration an isothermal cross-section of this system. In the subsolidus region of the CaO–Nd<sub>2</sub>O<sub>3</sub>–Nb<sub>2</sub>O<sub>5</sub> system the existence of 9 cross-sections that divide the discussed range of compositions into 10 ternary partial systems. Based on the XRD results, the type of coexisting phases in the partial subsystems has been established.