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REVIEW

of the doctoral dissertation of Houri Sadat Rahimi Mosafer, M.Sc., entitled: "Influence of transition metal content on structure and thermal expansion of Cal0.5 - x TM x (V04)7 (TM=Co, Ni, Cu) orthovanadates"

The doctoral dissertation submitted for evaluation by Ms. Rahimi Mosafer, M.Sc., concerns the crystal structure and its changes in a wide range of temperatures of a series of calcium orthovanadates substituted with transition metal ions. The work was carried out at the Institute of Physics of the Polish Academy of Sciences under the supervision of Prof. dr hab. Wojciech Paszkowicz *[professor, Ph.D., postdoctoral degree holder]* and assistant supervisor Dr Roman Minikayev *[Ph.D.]*.

The tested oxide materials crystallize in the structure of whitlockite-β-$Ca_3(PO_4)_2$ (space group R3c) and enable the incorporation of ions of other elements into the periodic structure of $Ca_3(VO_4)_2$, changing its properties and, depending on the valency of the ion, the overall structural formula. The work focuses on materials with substituted cobalt, nickel, or copper ions in a wide range of concentrations, also trying to determine the solubility limits. Materials in the form of sintered powders are examined using high-resolution powder X-ray diffraction and analyzed using the wide-angle refining of structure parameters known as the Rietveld method. The Ph.D. candidate analyzes in detail the changes in the crystal structure, possible admixtures of other phases, the location of transition metal ions substituting calcium ions on one of five different lattice sites, elements of structural disorder, anisotropic thermal expansion of the lattice, and determines the Debye temperature of the crystal. Analyses at room temperature are conducted in the 0-1 range of the x parameter of the general structural formula $Ca_{10.5-x}TM_x(VO_4)_7$ involving seven samples with different x concentrations, for each transition metal (TM). The scope of work is therefore very wide and includes analyzes of unsubstituted $Ca_3(VO_4)_2$ samples and substituted Ni and Cu for x = 0.5 in the low temperature range of 4-290 K (12 temperatures), at room temperature, and high temperatures up to 1100 K (18 temperatures). Laboratory measurements at high temperatures were performed for several concentrations of all substituted metals. For two metals, Co and Cu with a concentration of x = 0.5, high-resolution diffraction measurements were carried out at the European ESRF synchrotron in Grenoble (line ID22) at eight temperatures, from room temperature to 1100 K. These measurements enabled not only the analysis of thermal expansion but also a full analysis of the evolution of the structure. Such rich experimental material provides valuable source data for possible attempts at technological use of the tested materials. The author compares their properties with the literature results of studies on the substitution of $Ca_3(VO_4)_2$ with rare earth metal ions, which have been studied quite intensively in recent years. The interest stems from the interesting nonlinear optical properties of these materials that allow efficient generation

of luminescence with low environmental impact. Thus, they may have applications in both laser techniques and white LED technology.

The assessed dissertation begins with two introductory chapters describing the literature history of studying the crystal of the starting compound $Ca_3(VO_4)_2$, its structure, potential applications of derivative crystals, and the general possibilities and importance of research at high and low temperatures. The aim of the work is formulated here, including the stability and evolution of the structure of the proposed class of crystals (no phase transitions) and the determination of several technologically important properties of the tested phases (such as the temperature expansion coefficient). This part ends with a cursory review of the materials characterization techniques used, focusing on powder X-ray diffraction, the Rietveld method, and methods of analyzing the temperature expansion of the crystal lattice, which also enable the determination of the Debye temperature.

Chapter 3 describes the method of synthesis of the tested materials (obtained in cooperation with the CRISMAT laboratory, Caen, France) and their preparation for diffraction studies at various temperatures. The next chapters, 4,5, and 6 describe the results of the Rietveld analysis and the obtained evolution of the lattice parameters, respectively: at room temperature, at high temperatures, and low temperatures. The dissertation ends with a general discussion and conclusions.

The layout of the dissertation is quite logical, and reading is facilitated by a list of figures and tables in the text and a list of abbreviations. The paper is written in relatively correct English, and although the author made some linguistic errors, they did not make it impossible to understand the text. The reviewer feels called upon only to analyze the content of the dissertation and further ignores language issues.

As a reviewer, I list below a number of critical remarks and comments.

- On page 13, equation 2.4 is incorrect – the intensity of the reflection is proportional to the square of the structure factor and not, as the author writes, to the factor itself.
- In the section describing the basics of the Rietveld method (p.21), formulas 2.8-2.12 ignore the fact that in their denominator, instead of the measured intensity $Y_{obs}(i)$, there should be $Y_{obs}(i)$-backg(i), i.e. the subtracted measurement background (from the handle, capillary, etc.). However, this fact is taken into account in the FullProf software used and does not affect the results. Failure to subtract the background in the formulas for the procedure's convergence factors unjustifiably reduces the values of these factors, which no longer describe the quality of the fit. The problem was described in the paper by Hill,Fischer, J. Appl. Cryst. (1990). 23, 462-468.
- On page 22, the explanations for formula 2.13 are not precise. α_T is not defined anywhere, but $\alpha(T)$ is defined by formula 2.14. However, this formula is different from the general one given in Ch. 5 (eq. 5.1).

- At the turn of pages 22 and 23, the author writes an obviously false sentence: "In a state of thermodynamic equilibrium, these atoms remain immobile and exhibit no discernible movement or displacement". This is not equilibrium but a state of minimum energy.
- On page 23, the description of the Debye temperature (as transcribed from www.sciencedirect.com): "The Debye temperature (θ_D) describes the temperature of a crystal's highest normal mode of vibration", is jargon and awkward. Temperature characterizes the state of the body, not the mode. Maybe better: "The Debye temperature (θ_D) describes the temperature at which a crystal's highest normal mode of vibration is excited".
- On page 97 of Fig. B1, the high-temperature structure is poorly illustrated. The scale of the diffraction pattern is too flat, the image is blurred and there is no intensity scale. Such an illustration makes it impossible to assess the quality of the fit.

It is appropriate to add a general comment regarding the Rietveld method to the above remarks. In this method, it is difficult to estimate the actual error of the determined structural parameters. It is a method of gradient minimization of the objective function (the weighted sum of squares or moduli of deviations of the diffractogram calculated from the measured one) and the parameter error in the minimum is given on a purely statistical basis. However, the measured diffractogram should be corrected for all known factors that play a role in the measurement and the error in these corrections may shift the values of some parameters to the minimum. Such a change may well exceed a purely statistical error. This applies in particular to the peak intensity values converted into the values of the structure factor and parameters such as the positions of atoms in the unit cell, lattice site occupancy, and the parameter of atom deflections from the equilibrium position (Debye-Waller D-W factor). For example, incorrect intensity correction for X-ray absorption in the preparation may be partially corrected by the D-W factors (with which it is correlated), but as a result, it generates wide-angle oscillations of peak intensities that may change the values of the above-mentioned parameters to a minimum (e.g., cause the D-W factors to be negative at a minimum). Therefore, the results of the Rietveld method are only as good as the corrections used.

It is a pity that the author does not provide the values of the absorption coefficients of the tested materials or D-W factors anywhere in the dissertation. It seems that this would be appropriate in a doctoral dissertation, which should describe elements of methodological knowledge that could help future students of the method. This makes it impossible to assess whether, for example, in measurements of compressed pellets (Bragg-Brentano geometry), the assumption of infinite absorption is justified, or whether the correction described by Milberg is required (Journal of Applied Physics (1958) 29, 64) – correction not included in the FullProf software used.

The reviewer assumes that all corrections were appropriate, which is to some extent justified by the good convergence factors obtained. The absorption correction should also not affect the obtained network parameters or temperature expansion coefficients.

The above comments do not change the overall positive opinion about the paper, which provides a lot of new experimental data that may have technological applications. The Ph.D. candidate demonstrated proficiency in using the Rietveld technique and analyzing the results. Undoubtedly, the goal of the study outlined in the introductory chapters has been achieved. It is worth emphasizing the very large scope of the obtained source data and the good quality of the measurements themselves. They were partially described in three papers published in the journals Dalton Transactions, CrystEngComm, and Crystals. These are multi-authored works and the reviewer is only authorized to substantively evaluate the dissertation itself, which is an original work.

By positively assessing the reviewed work, I state that it meets the requirements for doctoral dissertations specified in Art. 13 of the Act on academic degrees and titles, as well as degrees and titles in the field of art of March 14, 2003 (Journal of Laws No. 65/2003, item 595, as amended), in the regulation of the Minister of Science and Higher Education on the detailed procedure for carrying out activities in doctoral and habilitation proceedings and in the procedure for awarding the title of professor of January 19, 2018 (Journal of Laws, item 261 of January 30, 2018) and customary procedures. Therefore, I appeal to the Scientific Council of the Institute of Physics of the Polish Academy of Sciences to accept the dissertation and admit Mrs. Houri Sadat Rahimi Mosafer, M.Sc., to the next stages of the doctoral process.

Zbigniew Kaszkur
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