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Wroclaw, 11.09.2023

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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 $Ca_{10.5-x}TM_x(V0_4)_7$ (TM=Co, Ni, Cu) orthovanadates"

The work was carried out under the supervision of Prof. dr hab. Wojciech Paszkowicz *[professor, Ph.D., postdoctoral degree holder]* and assistant supervisor Dr Roman Minikayev *[Ph.D.]* at the Institute of Physics of the Polish Academy of Sciences.

The doctoral dissertation prepared by Houri Sadat Rahimi Mosafer, M.Sc., concerns the structural analysis of new, multi-component oxides with a whitlockite-β-$Ca_3(PO_4)_2$ structure, carried out based on powder diffraction data obtained on a conventional powder diffractometer and synchrotron sources, in a wide temperature range (from 4 to 1150 K). Based on the results obtained from the refinement of crystal structures using the Rietveld method, thermal expansion and Deby temperatures were additionally determined. The research was supplemented with measurements of elemental analysis using the EDS method. The materials analyzed by the Ph.D. candidate were obtained by scientific partners at the Institute of Physics of the Polish Academy of Sciences and the CRISMAT Laboratory, Normandie Universite in Cean, France.

The work focused on three series of compounds with the structural formula $Ca_{10.5-x}TM_x(V0_4)_7$ ($0 \leq x \leq x_{lim}$), in which TM represents divalent transition metals: Co(II), Ni(II), Cu(II), while the solubility limit x_{lim} was determined from measurements of the V(x) relationship. **It should be emphasized that the results obtained for each family were published in renowned scientific journals from the JCR database, such as Dalton Transaction, CrystEngComm, Crystals.**

1. **H. S. Rahimi Mosafer,** W. Paszkowicz, R. Minikayev, M. Kozłowski, R. Diduszko, and M. Berkowski, "The crystal structure and thermal expansion of novel substitutionally disordered

$Ca_{10}TM_{0.5}(V0_4)_7$ (TM= Co, Cu) orthovanadates", Dalton Transactions 50, 14762-14773 (2021).

2. J. Sanchez-Martin, D. Errandonea, **H. S. Rahimi Mosafer,** W. Paszkowicz, R. Minikayev, R. Turnbull, M. Berkowski,J. Ibanez-Insa, C. Popescu, A. Fitch, P. Rodriguez-Hernandez, "The pressure and temperature evolution of the $Ca_3V_2O_8$ crystal structure using powder X-ray diffraction", CrystEngComm 25, 1240-1251 (2023).
3. **H. S. Rahimi Mosafer,** W. Paszkowicz, R. Minikayev, C. Martin, M. Kozlowski, O. Chukova, Y. Zhydachevskyy, and S. Nedilko, "Crystal Structure, Thermal Expansion and Luminescence of $Ca_{10.5-x}Ni_x(V0_4)_7$", Crystals 13, 853 (2023)

These are very good journals, representing a high scientific level. **It is important to highlight that in two works the Ph.D. candidate is the first, leading author.**

The doctoral dissertation by Houri Sadat Rahimi Mosafer, M.Sc., submitted for review, is a dissertation of 116 pages, consisting of eight chapters: Chapter 1 – an introduction to the $Ca_3(VO_4)_2$ family of compounds (8 pages); Chapter 2 – a description of the main research techniques used in the dissertation (11 pages); Chapter 3 – a description of synthesis methods with X-ray diffraction methodology (4 pages); Chapter 4 – the results of structural analysis for $Ca_{10.5-x}TM_x(VO_4)_7$ compounds (10 pages); Chapter 5 – the results obtained for $Ca_{10.5-x}TM_x(VO_4)_7$ compounds at high temperatures (10 pages); Chapter 6 – the results of structural analysis of $Ca_{10.5-x}TM_x(VO_4)_7$ performed at low temperatures (5 pages); then a discussion is presented (Chapter 7, 4 pages), and conclusions in Chapter 8. The whole is preceded by an abstract in Polish and English, a list of publications, and a list of figures, tables, and abbreviations used in the work. At the end of the dissertation, the author includes additional materials in supplements A, B, and C, along with an extensive list of references containing 103 items. **The paper's formatting is highly organized, and it has been meticulously edited with great thoughtfulness, resulting in a thorously enjoyable reading experience.**

The introduction (Chapter 1) contains all the necessary information to introduce the reader to the subject of the dissertation. They concern data on the $Ca_3(VO_4)_2$ family and the crystal structure of the whitlockite mineral, in which there are 5 positions occupied by the calcium atom M1-M5, with different coordination (the coordination number varies from 4 to 9). This allows for a wide modification of the chemical composition of these compounds through appropriate substitutions, aimed at obtaining appropriate physical properties. Thanks to the substitution of calcium with rare earth metal ions, efficient

second harmonic generators and materials for wLEDs (white light emitting diodes) were obtained. The rationale for testing these materials over a wide temperature range is also provided. One of them concerns the lack of reports on the behavior of calcium vanadium(v) oxides with admixtures of transition metals at high and low temperatures. In the final part of the chapter, the author defines the goals of the doctoral dissertation.

The doctoral dissertation aims to provide comprehensive structural data for a series of calcium vanadium(V) oxides (TCV) containing divalent cobalt, nickel, and copper ions; determination of phase stability and the maximum concentration of the dopant that can be introduced into the structure by substituting calcium ions; determination of the coefficient of thermal expansion and its behavior in these materials. The Ph.D. candidate emphasizes that this research fills the gap in knowledge regarding this group of TCVs.

The second chapter introduces the reader to the principles of X-ray diffraction, presents X-ray sources divided into X-ray tubes and synchrotron sources, and describes the Bragg-Brentano and Deby-Scherrer geometries used in powder diffraction. It describes the Rietveld method for refining the crystal structure, the basics of determining the coefficient of thermal expansion, and determining the Debye constant. The theoretical description aims to help in the analysis of the results presented in the dissertation, hence I rate it very well.

In the third chapter, Houri Sadat Rahimi Mosafer, M.Sc., presents the methods of synthesis of the tested materials and the methodology of the X-ray diffraction measurements performed. **It should be emphasized here that some of the research was carried out using synchrotron radiation at the ID22 station in Grenoble, which not only required preparing a suitable project but, most notably, "securing" measurement time in a competition organized by the station's Scientific Committee.** This confirms the timeliness, originality, and importance of the conducted research.

In the fourth chapter, the Ph.D. candidate performed measurements and phase and structural analysis for 16 materials. She quantitatively determined the phase composition, the solubility limit (x_{lim}), the dependence of the crystal lattice parameters as a function of composition, and determined the position in which the ions of the divalent impurity are located based on the analysis of interatomic distances. **One of the most important results obtained in this part of the dissertation is the identification of the M5 position as the place where the dopant is incorporated in the structure.** In Chapter 5, the Ph.D.

candidate presents high-temperature changes in lattice parameters for all 16 samples. For each composition, she determines the so-called inflection (refraction) temperature at which the c/a ratio changes; and determines the thermal expansion coefficients. For the compositions $Ca_{10}Co_{0.5}(V0_4)_7$ and $Ca_{10}Cu_{0.5}(V0_4)_7$, structure parameters are provided based on high-temperature diffraction of synchrotron radiation. It should be noted that for this type of materials, the agreement between synchrotron and traditional data is very high. Both the network parameters and T_{inf} are the same. Based on the observation of the change in the occupation of the M5 position, the Ph.D. candidate forms a hypothesis about the cause of changes in thermal expansion at high temperatures.

Three samples were selected for diffraction measurements at low temperatures performed at the ID22 synchrotron station: $Ca_3(VO_4)_2$, $Ca_{10}Ni_{0.5}(V0_4)_7$ and $Ca_{10}Cu_{0.5}(V0_4)_7$. The Ph.D. candidate performed a series of low-temperature measurements and an analysis analogous to the one in the previous chapter, determining the temperature dependences of the network parameters, interatomic distances, and determining the thermal expansion coefficient using the second-order expansion of the Grüneisen function. Deby temperatures were also determined for these three compositions. Summarizing this stage of the research, the Ph.D. candidate states that the Deby temperatures determined by her are only indicative and are not very precise, and further research is needed to determine the exact values. During the discussion at the public defense of the dissertation, I would like to hear what kind of research the Ph.D. candidate has in mind and the estimated range of uncertainty in the parameters she determined. Additionally, the introduction of a dopant into pure $Ca_3(VO_4)_2$ leads to a negative linear thermal expansion in the c direction, below 20 K for $Ca_{10}Ni_{0.5}(V0_4)_7$ and below 50 K for $Ca_{10}Cu_{0.5}(V0_4)_7$. Did the Ph.D. candidate wonder about the reason for such behavior of doped materials?

Chapter 7 presents a summary and discussion of the results in relation to literature data, with particular emphasis on thermal expansion and thermal expansion anisotropy. In doped crystals, above 800 K, there is a significant increase in volume thermal expansion, which the Ph.D. candidate explains by a decrease in the occupancy of the M5 position. Can the Ph.D. candidate expand on this topic during her defense? Figure 5.19 in Chapter 5 shows the change in the occupation of the M5 position by dopant atoms, which occurs only above 900 K. How was this occupation calculated? Was it by summarizing to unity with Ca occupancy, were both parameters determined independently? As the temperature increased, only the occupation of M5 and other positions occupied by calcium decreased. Can it be ruled out that

these changes are related to the dilution of electron density at high temperatures and not to a change in the occupation of a specific position? What strategy was used during refinement to minimize correlations between the M5 occupancy and the displacement parameters of the atoms located at this position? And finally, above 900 K, do the diffraction data show no changes that could confirm or exclude sample degradation processes?

To sum up the results presented in Chapters 4-6, I consider the most important achievements of the Ph.D. candidate to be:

- conducting a comprehensive structural analysis for a new series of compounds $Ca_{10.5-x}TM_x(VO_4)_7$, where TM stands for the transition metals Co(II), Ni(II) and Cu(II), using the Rietveld method,
- determination of the solubility limit of admixtures,
- determining the position in which dopant ions are incorporated,
- discovery of anisotropic changes in thermal expansion in doped materials,
- determining the relationship between the temperature of the trend change in the c/a course (the so-called inflection temperature) and the dopant concentration,
- determination of the Debye temperature based on the Grüneisen approximation V(T) for $Ca_3(VO_4)_2$, $Ca_{10}Ni_{0.5}(V0_4)_7$ and $Ca_{10}Cu_{0.5}(V0_4)_7$.

At the same time, I confirm that Ms. Houri Sadat Rahimi Mosafer, M.Sc., has achieved all the goals defined in the introduction. To achieve this, the Ph.D. candidate refined several dozen structure models for $Ca_{10.5-x}TM_x(VG_4)_7$ with different dopant concentrations and at different temperatures. **The results of the obtained calculations (partially presented in the dissertation and supplements A, B, and C) confirm the very good research skills related to solving and refining the crystal structure demonstrated by the Ph.D. candidate.**

The prepared doctoral dissertation is very well edited. However, it is understandable that in such studies, minor linguistic or editorial errors or awkward phrasings may occasionally occur. As my duty as a reviewer, I will provide a few examples for reference, although I do not anticipate discussing these during the defense.

Page 4. Error in the formula, it is $Ca_{2,85}Gd_{0.1}(V0_4)_7$, it should be $Ca_{2,85}Gd_{0.1}(V0_4)_2$.
On the same page, formatting failed in the last two formulas, it is VO4, and it should be VO_4.

Page 8. The fragment "..if the structure is remain at R3c, space group and what is maximum percentage of transition metal which can introduce, to this structure[44] is poorly worded. The same applies to the next sentence: "..structure stability are become of curiosity to check if there is any phase transition.."
Page 13. " causing the X-rays to diffract or scatter" should read "causing the X-rays to scatter and diffract"
Page 17. Instead of "to allows for", it should be „to allow for"
Page 25. Instead of "there are two different starting point", it should be "there are two different starting points"
Page 25. Reaction Imbalance (3.1)
Page 27. Instead of monochromataize it should be monochromatized
Page 39. Awkward phrase "it can not be estimated very precise about solubility limit"
Page 45. Instead of $Ca_{2.9}Me_{0.1}(PO_4)_2$ it should be $Ca_{2.9}TM_{0.1}(PO_4)_2$
Page 45. Instead of "investigation executed" it should be "investigation was executed", and instead of "which experimentally found", it should be "which was experimentally found"
Page 53. Instead of "material investigation", it should be "material investigated:
Page 57. Instead of "are selected to measure", it should be "were selected"
Page 66. Instead of coeeficient - coefficient
In Supplements A, B, and C, the Ph.D. candidate presented the results of refining the crystal structure, such as: lattice parameter values, atomic positions, and interatomic distances. Often giving numerical values without rounding to significant figures, e.g., 0.26760(356); 0.00000(0).

I would like to emphasize that the above comments do not in any way affect the very positive assessment of the results obtained by Ms. Houri Sadat Rahimi Mosafer, M.Sc. Please treat them primarily as guidance that may be useful during further research.

To sum up, the doctoral dissertation submitted for review presents a high scientific level and constitutes a valuable contribution to the field of research on compounds for applications in optoelectronics. The subject matter is up-to-date, and the research results and their interpretation are presented correctly. In connection with the above, I declare that the doctoral dissertation of Houri Sadat Rahimi Mosafer, M.Sc., entitled: "Influence of transition metal content on structure and thermal expansion of $Ca_{10.5-x}TM_x(V0_4)_7$ (TM=Co, Ni, Cu) orthovanadates" meets the requirements set out in Art. 187 of the Act of July 20, 2018 "Law on Higher Education and Science", consolidated text published in the Journal of Laws: Journal of Laws 2022 item 574, and I apply to the Scientific Council of the Institute of Physics of the Polish Academy of Sciences to allow Houri Sadat Rahimi Mosafer, M.Sc., to publicly defend her doctoral thesis.

Sincerely,

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