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Review of the doctoral dissertation of **Houri Sadat Rahimi Mosafer**, M.Sc.
Dissertation title: **"Influence of transition metal content on structure and thermal expansion** of $Ca_{10.5-x}TM_x(VO_4)_7$ **(TM=Co, Ni, Cu) orthovanadates".**
Supervisor: prof. **Wojciech Paszkowicz** *[professor]*
Assistant supervisor: dr **Roman Minkayev** *[Ph.D.]*
Work done at the **Institute of Physics of the Polish Academy of Sciences**

In accordance with legal requirements, I declare that I am qualified to conduct the review. I have held the position of chemistry professor since 2007. In my scientific work, I perform diffraction studies using both laboratory and synchrotron X-ray sources. I specialize in structural research on polycrystalline materials and single crystal samples.

I also declare that I performed the review personally without violating the rights of third parties.

Work organization and general comments

The doctoral dissertation is written in English. The work has a classic layout, after abstracts in Polish and English, there is a list of the author's scientific achievements, a table of contents, a list of tables and figures, and a list of abbreviations and symbols.

Then there are three chapters of theoretical and literature introduction discussing the family of $Ca_3(VO_4)_2$ compounds, a list of research techniques, and a discussion of the details of syntheses and tests in non-standard conditions. The following Chapters 4, 5, and 6 discuss the results of structural studies of $Ca_{10.5-X}TM_X(VO_4)_7$ compounds at room temperature, high and low temperatures. The research is summarized in the General Discussion and Conclusions chapters. An

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important element of the paper are the three chapters of Supplements A, B, and C, which are an archive documenting all the research results presented in chapters 4 - 6. Thanks to this, the reader can easily find data documenting the facts discussed in the work, and the chapters describing the research results become more transparent and are not too extensive. The dissertation ends with a list of references containing 103 items.

Discussion of methods and results

The materials examined in the doctoral thesis are relatively new, as they were described in the literature only in 1965. They crystallize in the R3c symmetry group, and despite their apparent simplicity, they create quite a complex structure due to high symmetry and high lattice parameter values (a, c = 10.81 and 38.03 Å). It contains 5 different positions occupied by Ca cations and TM or RE metals and three different polyhedron coordination of V atoms, and the Z number has a rare value of 21!. The compound is durable, has a high melting point and its space group predestines it for optical applications such as generating the second harmonic, a material for building lasers, and attempts have been made to use it as a pigment. Moreover, good-quality crystals can be obtained using the Czochralski method.

The study includes structural tests based on powder data, tests of thermal expansion coefficients in the range of low and high temperatures, and estimation of the Debye temperature.

In Chapter 2 we will find an interesting description of the basics of X-ray diffraction and a description of the production of X-rays using X-ray tubes and synchrotrons. Next, there is a description of experiments using polycrystalline preparations, including the Bragg-Brentano geometry (with the Johansson monochromator) and the Debye-Scherer geometry (important due to the experiments performed at the ESRF in Grenoble). Due to the importance of structural research, the basics of the Rietveld method are discussed quite extensively in the work. At the end of the chapter, the theoretical basis and methods of determining the thermal expansion coefficients and Debye temperature are discussed.

The brief Chapter 3 provides details of the methods for obtaining preparations; in addition to the Czochralski method, methods based on reactions of components in the solid phase were used for a wide range of compositions. Next, we can learn the technical details of how samples are prepared for diffraction experiments. Such information, often overlooked, can sometimes be invaluable when trying to reproduce experimental results.

Chapter 4 describes the structural tests of the preparations at room temperature. Some samples turned out to be two- or three-phase. The Rietveld method is capable of providing valuable information in such cases, including the estimation of the percentage composition of each phase. For three families of compounds, with Co, Ni, and Cu cations in specified quantities, complex and meticulously detailed calculations were carried out, requiring significant effort and attention to detail. The obtained results were analyzed in terms of phase composition, the type of position selected by the TM atom, changes in lattice parameters, and the size of the average M-O size for the 5 positions of Ca atoms. The results show interesting, logical relationships that can be related to the elemental composition, and more specifically to the atomic radii of Ca, Co, Ni, and Cu. With appreciation for the diligence and professionalism of the researchers, I declare that I have no objections to the presented results.

Chapter 5 is the study of TCV-TM compounds as a function of temperature. The methodology used is fully justified. Interesting relationships of a,c, and V as a function of composition and temperature were observed. These changes can be correlated with changes in thermal expansion coefficients. Interesting anomalies were observed around the temperature of approximately 800C, slightly depending on the composition. To clarify it, research was carried out using synchrotron radiation. Studies using laboratory and synchrotron diffraction data were compared, the comparison indicates a much better quality of synchrotron data in structural studies. However, laboratory data prove to be completely sufficient for most physicochemical applications. The studies showed a reduction in the number of TM atoms in the M5 position. However, it has not been possible to determine where they are moving.

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Chapter 6. For three samples $Ca_3(VO_4)_2$, $Ca_{10}Ni_{0.5}(VO_4)_7$, and $Ca_{10}Cu_{0.5}(VO_4)_7$, low-temperature measurements in the range from 4K to 290K were performed at the ESRF Grenoble synchrotron facility. The measurements were processed computationally using the Rietveld method. The preparations remained stable within this temperature range, and a thorough analysis revealed an interesting anomaly in the form of an initial decrease in the c/a ratio for all samples in the range of 4K to 30 (or 50K), followed by a subsequent increase. Average M - O values were analyzed, but no clear trends were observed. Graphs for individual M_i-O_j values are presented in Supplement C, however, after several attempts, I agree with the author's conclusion! Temperature changes in thermal expansion coefficients were presented and Debye temperatures were determined for the tested materials.

Comments and evaluation of work

The illustrations are of very good quality, the paper is written in very good English, has a clear, logical layout, and is very easy to read. The study contains many interesting results. They are logically arranged and easy to find. The research and the publications based on it can be treated as highly reliable recipes on how to obtain the planned value of physical properties for materials such as $Ca_3(VO_4)_2$, $Ca_{10\cdot5\cdot x}Nix(VO_4)_7$, $Ca_{10\cdot5\cdot x}Co_x(VO_4)_7$ and $Ca_{10.5-x}Cu_x(VO_4)_7$.

Ms. H.S. Rahimi Mosafer has very good scientific achievements, including 3 positions. It should be noted that the journals Dalton Transaction and CrystEngComm are among the leading journals in the field of chemistry and materials chemistry.

The purpose of the study was clearly outlined and achieved. It used modern research methods, including the use of the best synchrotron X-ray sources at ESRF Grenoble.

Questions and uncertainties.

Page 40, Table 4.7

How can one explain the high value of x_{EDX} for Cu at x_{nom} =1?

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On the same page, in the following sentence Cu was replaced by Ca: At higher concentrations, the M3 and M2 sites start to host Ca ions after achieving almost full occupancy of the M5 site [8]. Similarly, on page 62, the reference to Figures 6.3-c, 6.4-c and 6.5-c refers to Figures 6.3-b, 6.4-b and 6.5-b.

In Figures 4.9-11 we have the estimated errors: for x=0.16 Δ<M-O> and x=0.78 Δx. Would it be very difficult to provide errors for all values of x, and how Δx was determined? The M4-O values also show a clear change as a function of x, can this be explained?

Summary and final assessment

Minor ambiguities or a few editorial imperfections do not detract from the very good impression nor from a very good assessment of the work.

In my opinion, the doctoral dissertation of Ms. **Houri Sadat Rahimi Mosafer**, M.Sc., meets all the requirements for the doctoral dissertation contained in statutory provisions (Article 187 of the Act of July 20, 2018, Law on Higher Education and Science (Journal of Laws of 2022, item 574, as amended)).

Therefore, I am requesting that Ms. **Houri Sadat Rahimi Mosafer**, M.Sc., be admitted to the next stages of her doctoral studies.

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