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Title: High-sensitive luminescent thermometers based on formate hybrid perovskites containing $Cr^{3+}$ ions

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# Abstract

The dynamic development of areas such as science, industry, and medicine requires the implementation of highly accurate methods of monitoring the temperature. This parameter is directly related to a wide range of physical and chemical properties as well as strongly affects the dynamics of many phenomena. Even though conventional temperature sensors provide sufficient characteristics for the majority of the undemanding applications, the specific scientific, industrial, and biomedical sectors require the use of highly sensitive non-contact and remote sensing systems.

Conventional contact thermometers are based on the temperature-induced change of the physical parameters, e.g., thermal expansion in common liquid-based thermometers or electric resistance in thermistors. Currently, the most commercially available non-contact sensing approach is thermal imaging. This method is based on the analysis of infrared radiation intensity emitted and reflected by the measured object. Luminescent thermometers, in turn, use temperature-dependent spectroscopic properties. There are three standard approaches to a luminescence-based temperature detection: analysis of a change in luminescence decay kinetics; monitoring the spectral shift of an emission band; and the comparison of the emission intensity of two spectrum ranges characterized by different temperature dependencies. The last one is known as a ratiometric approach and has become the most commonly reported method.

Although there are a number of thermometric compounds, the vast majority of materials are based on inorganic compounds, usually doped with lanthanides.[1] However, the group of metal-organic frameworks (MOFs) are promising material for luminescent thermometry.[2,3] MOFs may exhibit several interesting properties simultaneously, and their characteristics can often be tuned by the substitution of the building blocks. Among various MOFs, the group of materials with perovskite stoichiometry containing formate ($HCOO^-$) linkers, doped with chromium(III) ions ($Cr^{3+}$), is particularly noteworthy. Their high stability as well as reliability and accessibility of preparation, overcoming most of the halide-based compounds, make these materials a valuable choice for studies concerning the influence of chemical composition on spectroscopic and, subsequently, thermometric properties. Depending on the chemical composition of the analyzed materials, including the type of amine, the type of metal, and the concentration of chromium(III) ions, it is possible to obtain different spectroscopic properties related to the $Cr^{3+}$ luminescence. The local environment of the chromium ions can be described by the crystal field strength, which induces the dominant emission type of the $Cr^{3+}$ ions: narrow spin-forbidden $^2E_g \rightarrow {}^4A_{2g}$ or broad spin-allowed $^4T_{2g} \rightarrow {}^4A_{2g}$ transitions. Hybrid compounds

based on $Cr^{3+}$ ions exhibit a significant temperature dependence of their luminescent properties, which has become a starting point for their application in the field of luminescent thermometry. The observed influence of chemical composition on luminescent properties also affects their thermometric characteristics.

The primary objective of this work is to describe the relationship between the chemical composition of hybrid formate materials doped with $Cr^{3+}$ ions, described by single- and double-perovskite stoichiometry, and their spectroscopic properties as well as, consequently, their thermometric performance. In this dissertation, 5 series of compounds differing in chemical compositions were synthesized, analysed, and further described in a series of five thematically coherent publications **P1-P5**. Among the investigated series, two of them focus on materials with double-perovskite stoichiometry (**P1-P2**), while others are devoted to single-perovskite-like materials (**P3-P5**). Taking included works into account, the analysis of the 38 individual samples has been performed.

The study provides a detailed description of their structural, phonon, and spectroscopic properties as well as their relation to chemical composition, which was tuned by modifying the fundamental building blocks of the hybrid frameworks. Based on the collected data, the general relations between crystal-field strength, the type of metal ions and organic cations, dopant concentration, and resulting luminescent and thermometric behaviour were established. Thermometric analyses demonstrated the possibility of achieving high relative sensitivities, reaching up to $3.91\%\cdot K^{-1}$ at 140 K (ratiometric method) and $5.14\%\cdot K^{-1}$ at 143 K (lifetime-based method). Through multiparametric thermometric analysis, various sensing strategies were systematically compared, enabling further optimization of thermometric model development. The proposed prototype thermometric setups, operating under steady-state conditions and in the time domain, illustrate the potential of the investigated materials as cryogenic temperature sensors.