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Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Glass formation and mechanical properties of melt-quenched glasses of mixed metal node Zn/Co ZIF-62

Malwina Stepniewska[1], Chao Zhou[1], Ang Qiao[2], Yuanzheng Yue[1,2]

[1]*Department of Chemistry and Bioscience, Aalborg University, DK-9220 Aalborg, Denmark*

[2]*State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China*

*Presenting author. E-mail: mst@bio.aau.dk

Recently, the newly-discovered melt-quenched Zeolitic Imidazolate Framework (ZIF) glasses have been attracting a lot of attention owing to their particularly high thermal, mechanical and chemical stability [1-4]. ZIF structures are built analogously to zeolites, but ZIF consists of transition metal ions that are bonded to imidazolate ligands, creating a three dimensional framework. However, for ZIF crystals, there are many questions that need to be answered. For instance, what is the microscopic mechanism of the ZIF glass formation? How does the chemical composition influence ZIF glass properties?

In this work, we explore the impact of the change of metal ion type on the glass formation of ZIF-62 ($Zn_{1-x}Co_x(Im)_{1.75}(bIm)_{0.25}$. This is done by substituting zinc ions for cobalt ions during synthesis of the ZIF-62 crystal and by characterizing the morphology of crystalline powders obtained during synthesis using Scanning Electron Microscopy. 1H and 13C Liquid Nuclear Magnetic Resonance measurements were conducted to determine the content of two types of organic ligands in both crystalline and amorphous phases, whereas X-ray Photoelectron Spectroscopy measurements were performed to detect any possible bond changes. Inductively Coupled Plasma Mass Spectrometry was performed to quantify the content of metal nodes in the frameworks. The melting temperature of ZIF-62 crystals, as well as the glass transition temperature of ZIF-62 glasses have been determined using Differencial Scanning Calorimetry. Thermogravimetry was used to observe desolvation and decomposition. Both nanoindentation and microindentation were applied to measure mechanical properties of ZIF-62 glasses. We have found that substitution of second transition metal ions for Zn greatly lowers the glass forming ability of ZIF-62. The structural origin of this phenomenon has been discussed in this work. Furthermore, we have discovered the Zn/Co has only minor impact on the properties.

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