frontiers in Materials

EDITORIAL
published: 14 March 2022
doi: 10.3389/fmats.2022.873553

Editorial: Recent Advances in Low-Positive, Zero, and Negative Thermal Expansion Materials: Fundamentals and Applications

Bojan A. Marinkovic[1], Mary Anne White[2]*, Jun Chen[3] and Andrea Sanson[4]*

[1]Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, Brazil, [2]Department of Chemistry, Dalhousie University, Halifax, NS, Canada, [3]Department of Physical Chemistry, University of Science and Technology Beijing, Beijing, China, [4]Department of Physics and Astronomy, University of Padua, Padua, Italy

Keywords: negative thermal expansion (NTE), zero thermal expansion, coefficient of thermal expansion (CTE), ceramics, composites, applications

Editorial on the Research Topic

Recent Advances in Low-Positive, Zero, and Negative Thermal Expansion Materials: Fundamentals and Applications

Most materials expand as the temperature increases, giving issues such as changes in properties of devices arising from their dimensional changes (e.g., materials used for interferometry), and fracture due to thermal stress exceeding material strength. Although contraction of some solids with increase of temperature had been reported more than 90 years ago (Sosman, 1927; Adenstedt, 1936), the 1996 report (Mary et al., 1996) of negative thermal expansion in a ceramic over a wide temperature range raised the exciting promise of materials that could be tailored to have near-zero thermal expansion. The field of controlled thermal expansion has blossomed over the intervening decades, leading us to propose this Special Issue of Frontiers in Materials, dedicated to the topic of "*Recent Advances in Low-Positive, Zero, and Negative Thermal Expansion Materials: Fundamentals and Applications*."

Low-positive, near-zero and negative thermal expansion materials are relatively rare. Although these unusual thermal expansion properties have been reported for a few materials, systematic studies of the physical mechanisms and crystallographic studies concerning these properties are still in development. An increased interest in this exotic class of materials has arisen from newly discovered materials showing these properties near room temperature or over a wide temperature range.

The types of materials exhibiting low-positive, zero, and negative thermal expansion are exemplified in the papers in this special issue, from inorganics and ceramics to macroscopic structures including composites. The range of insightful investigative techniques includes theoretical approaches [analytic studies; numerical investigations; lattice dynamics and thermal expansion combining density functional theory (DFT) and quasi-harmonic approaches] and experimental methods, with the latter including crystallography, dilatometry, thermoelasticity, electrical and thermal transport properties, optical properties, and methods of synthesis and consolidation.

A study by Sun et al. from Zhengzhou University in China provides theoretical insights concerning CuSCN, a new type of inorganic hole-transporting semiconductor with a wide bandgap (>3.4 eV), that is attracting much attention in the fabrication of perovskite solar cells. This work reveals the mechanisms of the unusual thermal expansion in CuSCN and how it influences its bandgap, as a function of the phase of CuSCN, and temperature. Their calculations predict that α-CuSCN has a direct bandgap, which increases slightly with

OPEN ACCESS

Edited and reviewed by:
Valeria Cannillo, University of Modena and Reggio Emilia, Italy

****Correspondence:***
Bojan A. Marinkovic
bojan@puc-rio.br
Mary Anne White
Mary.Anne.White@dal.ca

Received: *10 February 2022*
Accepted: *17 February 2022*
Published: *14 March 2022*

Citation:
Marinkovic BA, White MA, Chen J and Sanson A (2022) Editorial: Recent Advances in Low-Positive, Zero, and Negative Thermal Expansion Materials: Fundamentals and Applications. Front. Mater. 9:873553. doi: 10.3389/fmats.2022.873553

increasing temperature, whereas β-CuSCN has an indirect bandgap at low temperature, which converts to a direct bandgap near the temperature of 375 K due to the strong positive expansion in the *ab* plane. Full understanding of the band gap of CuSCN is critical for its use in solar cells.

A promising family of materials with negative and near-zero thermal expansion, of general formula $A_2M_3O_{12}$, where A is a trivalent cation in the range Al^{3+} to Dy^{3+} and M is generally W^{6+} or Mo^{6+}, offers considered flexibility of chemistry and properties. These materials are reviewed in a study, Marinkovic et al., co-led by Bojan Marinkovic from Pontifical Catholic University of Rio de Janeiro, Brazil, and Mary Anne White from Dalhousie University in Canada, and their collaborators in Brazil, Ecuador and Switzerland. This extensive review includes the history of these materials, and presents the current understanding of the mechanism of their unusual thermal expansion, and related factors including hydroscopicity and the monoclinic to orthorhombic phase transition. Other properties, including thermomechanics, thermal and ionic conduction and optical properties, are presented in terms of the current state of understanding, and challenges and opportunities for applications. One of the largest challenges is the production of monoliths, and the state-of-the art methods for consolidation are summarized in the study.

A collaborative study from the United States led by Jason Hancock, including researchers from University of Connecticut and MIT, Curry et al., investigated soliton generation in negative thermal expansion materials. Strain solitons have been observed in 2D materials and substrates, and arise from lattice relaxation in response to ultrafast heating, a process which is sensitive to the thermal expansion coefficient. In this investigation, the authors present the results of numerical studies which show that the emerging solitons are qualitatively different depending on whether the material exhibits positive or negative thermal expansion. This work presents the first assessment of negative thermal expansion materials as acousto-optic transducers for strain wave generation. The novel case of negative thermal expansion gives rise to a nearly periodic soliton train with chirped profile that is devoid of an isolated shock front. While both the negative and positive thermal expansion cases produce the same number of solitons as anticipated, the negative thermal expansion case is found to deliver a soliton train with more uniform distribution of strain over the solitons present, and significantly higher spatial frequencies at early times. The work reveals potential advantages of negative thermal expansion transducers in retaining a periodic strain texture capable of propagating over long distances in functional acousto-optic devices. This theoretical study provides a strong motivation for future experimental investigations of strain solitons in negative thermal expansion materials.

A study, Grima-Cornish et al. led by Joseph Grima of the University of Malta, including collaborators there and in the United Kingdom, investigated macroscale construction of systems with controlled thermal expansion coefficients. These systems were inspired by the studies of hexagonal honeycombs which exhibit anomalous Poisson ratios. Their analytic investigation presents re-entrant, standard non-re-entrant and hybrid honeycombs built from vertical and slanting ligaments with different thermal properties and examines the macro-scale thermal expansion. They show that for re-entrant systems, overall negative thermal expansion can result when the ligaments exhibit positive thermal expansion, and negative thermal expansion does not necessarily result when the ligaments exhibit negative thermal expansion. On the other hand, non-re-entrant honeycombs made from positive thermal expansion materials cannot exhibit negative thermal expansion in any direction, nor does the use of negative thermal expansion ligaments guarantee overall negative thermal expansion. A very exciting finding is that it is possible to construct honeycombs with zero thermal expansion in specific directions.

The papers in this research topic provide a snapshot of current work concerning materials with low or negative thermal expansion coefficients, from their fundamentals to their applications. These studies form a framework for potential applications of negative and near-zero thermal expansion materials and highlight future challenges for materials researchers.

AUTHOR CONTRIBUTIONS

MAW—writing—original draft preparation; BM—writing—review and editing; AS—writing—review; JC—writing—review.

REFERENCES

Adenstedt, H. (1936). Studien zur thermischen Ausdehnung fester Stoffe in tiefer Temperatur (Cu, Ni, Fe, Zinkblende, LiF, Kalkspat, Aragonit, NH4Cl). *Ann. Phys.* 418, 69–96. doi:10.1002/andp.19364180105

Mary, T. A., Evans, J. S. O., Vogt, T., and Sleight, A. W. (1996). Negative Thermal Expansion from 0.3 to 1050 Kelvin in ZrW 2 O 8. *Science* 272, 90–92. doi:10.1126/science.272.5258.90

Sosman, R. B. (1927). *Properties of Silica*. New York: Chemical Catalogue Company.

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.