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# Negative thermal expansion coefficient materials: From basics to applications, recent advances in solid oxide cells and future perspectives

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#### ABSTRACT

Negative thermal expansion has always interested scientists as an extraordinary physical property. Understanding this specific phenomenon allows to design and synthesize materials with abnormal, anisotropic, nearzero, or negative expansion. In effect, these materials find applications in many branches of science like mechanics, optics, micro- and nanoelectronics, magnetics, and medical and chemical applications. Since the great majority of these materials are electrical insulators, they did not find practical applications in electrochemistry. However, recently a new group of perovskite-based materials was discovered which gave vast opportunities to utilize such materials in fuel cell technology giving outstanding possibilities to improve and enhance their electrical, thermomechanical, and electrochemical properties. Therefore, the most limiting factor, which is the long-term stability, may be mitigated leading to improved electrolyte/electrode durability which enables future perspectives possibly allowing for faster commercialization of the technology.

In this review article, we present a general insight into thermal expansion and its physical explanation along with many examples of materials with negative expansion, exhibiting different crystal structures. Experimental techniques for thermal expansion coefficient evaluation are summarized and widely discussed. In the main part of the article, many applications of materials with negative expansion are presented, focusing on recent advances in electrochemistry, mainly as composite electrodes with negative thermal expansion materials addition, which improves the electrochemical performance of solid oxide cells. In the summary, we present drawn conclusions and discuss future perspectives as a widely and rapidly developing branch of electrochemistry.

#### 1. Introduction

Materials have been present in humans' lives for centuries to improve the quality of life. The first wrought metal tools from basic minerals are dated even to around 9000 BCE [1]. In general, materials can be defined by their state of matter, fragility, hardness, or resistance to different external conditions like temperature and pressure. To properly describe the properties of the materials, different physical quantities are used. Beginning with macroscopic quantities i.e. volumetric size, we can roughly describe the object. On the other hand, a lot of optical, electrical, and magnetic properties are investigated at the level of molecules, atoms, or electrons. However, almost each physical property changes with the temperature. Many years of research and a lot of experiments allowed us to find suitable applications involving the properties changes with the temperature. For instance, nowadays almost every bridge has expansion joints that are used to absorb thermal expansion giving a possibility to "breathe" what prevents cracks formation, degradation, and eventually collapse [2]. Similar thermal expansion absorbing solutions are used in railway tracks [3] and piping systems [4]. The great majority of known materials are expanding when temperature increases. Interestingly, in the last decades, state-of-the-art negative thermal expansion materials (NTEs) have been developed and

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used in many applications, especially in electronic and electrochemical devices [5–7].

In general, from the physical point of view, the nature of thermal expansion can be explained by an anharmonic oscillator [8], in which potential energy on the mean separation of a pair of atoms at a certain temperature T can be expressed by:

$$U(x) = ax^2 - bx^3 - cx^4$$
 (1)

where *a*, *b*, *c* are positive constants,  $ax^2$  are typical harmonic oscillations, the  $bx^3$  the term represents the mutual repulsion asymmetry of the atoms, whereas the softening of the vibration at large amplitudes is expressed by the term  $cx^4$ .

Using the Boltzmann distribution function, the average displacement of x according to their thermodynamic probability can be calculated as follows:

$$\langle \mathbf{x} \rangle = \frac{\int\limits_{-\infty}^{\infty} \mathbf{x} e^{[-\beta \mathbf{U}(\mathbf{x})]} d\mathbf{x}}{\int\limits_{-\infty}^{\infty} e^{[-\beta \mathbf{U}(\mathbf{x})]} d\mathbf{x}}$$
(2)

Where  $\beta = 1/k_BT$ , ( $k_B$  is the Boltzmann constant), however, only anharmonic terms (in this case  $bx^3$  in the equation give nonzero values, since integrals with even contributions vanish. Therefore, after calculations, we can write:

$$\langle \mathbf{x} \rangle = \frac{3\mathbf{b}}{4\mathbf{a}^2} \mathbf{k}_{\mathbf{B}} \mathbf{T} = \alpha \mathbf{T}$$
(3)

Generally, the property of thermal expansion of certain materials can be used to improve the performance or quality of different devices. On the other hand, scientists struggle with thermal expansion coefficient (TEC) mismatch in electrochemical devices such as solid oxide cells, where the TEC of the electrolyte material varies from the TEC of the anode and cathode. In effect, upon heating and cooling, unwanted strain occurs and damages the device, preventing it from commercial applications. Interestingly, strain also may be induced in a thin film intentionally, to improve the electrochemical properties [9,10]. Therefore, the application of materials with negative thermal expansion may be useful in terms of potential solutions for the mentioned problems.

The NTE materials have gathered vital attention for their ability to restrain thermal expansion in composite materials. However, their implementation as additives is hampered by several limitations. Many NTE materials like some perovskite-based compounds, ZrW<sub>2</sub>O<sub>8</sub> and ScF<sub>3</sub> need precise conditions for their synthesis, including specific temperature treatments, high-purity precursors, and controlled atmospheres. These precise synthesis conditions can limit reproducibility and largescale production of NTE materials. Some NTE materials require expensive raw materials (e.g. scandium-based compounds) for their synthesis, making them infeasible for industrial applications and increasing production costs [11]. Integrating NTE materials presents compatibility issues in composite with conventional materials which is because of the difference between their chemical stability, thermal behavior, and mechanical properties resulting in phase separation, interfacial stress, and even material degradation over time [12,13]. The negative thermal expansion of many NTE materials is exhibited in a specific temperature range only. Beyond this temperature range, these NTE materials may undergo positive expansion or phase transformations, limiting their functionality in applications with wide temperature variations [14]. Some NTE materials e.g. ZrW2O8 etc. are sensitive to environmental conditions such as high pressures or moisture, which lead to reduced performance and structural instability [15]. Attaining a uniform dispersion in metallic or polymeric matrices of NTE additives can be challenging and poor dispersion may result in thermal expansion mitigation or localized stress concentrations which affect the overall performance of the composite [16]. Therefore, further research is needed in NTE materials to address these limitations in material modifications for improved stability, cost-effective synthesis routes, and optimized processing techniques for composite.

## 2. The nature of thermal expansion

From the physical point of view, the thermal expansion of gas, liquid, or solid material can be generally expressed by eq. (4):

$$\alpha_{\rm V} = \frac{1}{\rm V} \left( \frac{\partial \rm V}{\partial \rm T} \right)_{\rm p} \tag{4}$$

Where  $\alpha_V$  is the volumetric coefficient of the thermal expansion, *V* is the volume  $\partial V / \partial T$  is the volume derivative over temperature *T*, and subscript *p* denotes the constant pressure upon expansion. However, despite the thermodynamical derivation being correct, it is impossible to measure infinitely small temperature changes at constant pressure, therefore, on a real laboratory scale we need to make some assumptions. In the case of solid materials, which are the object of interest in this article, one can ignore the effects of pressure exerted on the material, and if we know the temperature and volume changes explicitly, the equation may be written as follows:

$$\alpha_{\rm V} = \frac{1}{\rm V_0} \frac{\Delta \rm V}{\Delta \rm T} \tag{5}$$

Where  $\Delta V$  and  $\Delta T$  are changes in volume and temperature respectively, and  $V_0$  is the initial volume.

Assuming that the isotropic materials expand the same way in each spatial direction and that V may be approximated as cubed length  $L^3$ , one can also write:

$$\alpha_{\rm V} = 3\alpha_{\rm L} \tag{6}$$

where  $\alpha_L$  is linear thermal expansion coefficient. The majority of the reported TECs are given as linear values, therefore, if not stated otherwise, the authors' mean  $\alpha_L$  as

$$\alpha_{\rm L} = \frac{1}{L_0} \frac{\Delta L}{\Delta T} \tag{7}$$

Also, if not stated otherwise, the  $\alpha_L$  is just denoted as  $\alpha$ , meaning isotropic one-dimensional expansion. The majority of known materials expand during heating, whereas some of them shrink, which suggests their negative TEC and therefore may be called negative thermal expansion materials.

#### 2.1. Positive thermal expansion and near-zero expansion

Phonon modes, which are quantized vibrations of the crystal lattice, may have different amplitudes, frequencies, and wavelengths. Assuming hypothetic stoichiometric MO oxide, upon heating the longitudinal M-O-M bonds are increasing, promoting interatomic distances which in effect give a positive TEC, as an effect of increased effective metal-metal distance, which is schematically shown in Fig. 1a. The great majority of known materials exhibit TEC values greater than zero as an effect of the mentioned bonds. Metals, ceramics, glasses, organic materials, and many others expand upon increasing temperature. Their TECs span within more than one order of magnitude between room temperature up to around 1000 °C [17]. For instance, copper has a TEC of around 17  $\times$  10<sup>-6</sup> K<sup>-1</sup> at room temperature and around 25  $\times$  10<sup>-6</sup> K<sup>-1</sup> at 1000 °C [17]. Barium carbonate exhibits TEC around 300  $\times$  10<sup>-6</sup> K<sup>-1</sup> through the c-axis between 820 °C and 960 °C [18].

There are many materials that exhibit very low TEC, called zero thermal expansion materials (ZTEs). This may be caused either by isotropic near-zero expansion, or averaged expansion from three crystallographic axes which may be positive and negative. According to a review done by Roy et al., [19], three structural features have to be



Fig. 1. a) M-O-M bonds for longitudinal vibrations responsible for positive TEC, where the effective metal-metal distance increases, b) M-O-M bonds for transverse vibrations responsible for negative TEC, where the effective metal-metal distance decreases.

fulfilled to have almost zero TEC. First of all, in the crystal lattice, there should be linked polyhedra which are strongly bonded in all spatial dimensions, to prevent the bond length changes. Secondly, low packing density is needed to absorb the thermal energy in transverse vibrations perpendicular to the bond directions. Lastly, ferroelectric or ferromagnetic domains are necessary to compensate for volumetric changes caused by changes in thermal energy. Interestingly, the near-zero thermal expansion is a mixture of contradicting mechanisms of positive and negative expansion. For example, the compensating effects were reported by Gao et al., in the layered structure of  $Ta_2Mo_2O_{11}$  [7], where along the layers, the material shrinks and the interlayer distance increases during increasing temperature giving in effect a perfectly balanced near-zero TEC. The other example may be a ZTE semitransparent glass-ceramic called "Zerodur", between 20 °C - 600 °C has TEC equal to  $0.12 \times 10^{-6} \text{ K}^{-1}$  [19]. Thanks to these almost zero expansions in a wide temperature range it may be applied in optics, for example as a reflector in a telescope. One of the most common metal alloys exhibiting near-zero TEC is Invar (from 'invariant'), which is an alloy consisting of around 65 % of iron and around 35 % of nickel [20]. There are also several alloys, that are reported to have exact zero expansion  $(0K^{-1})$ , e.g.  $Fe_{63}Ni_{32}Co_5$ ,  $Fe_{70}Pd_{30}$ , or  $Fe_{37}Co_{52}Cr_{11}$  [21]. These thermal anomalies of both positive and negative TEC have gained much attention last time. Understanding these phenomena allowed to design and synthesize many materials in a precise controllable way offering many possibilities to use them commercially. In general, ZTE materials find applications in mirror fabrication (optics) [22], highprecision devices [23], mechanical timers, engine valves [24], and medical implants [25].

#### 2.2. Anisotropic thermal expansion

The TEC also may be anisotropic, where the coefficient differs along each crystallographic axis. An interesting example may be an orthorhombic Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> which exhibits averaged linear change close to zero, namely  $1.5 \times 10^{-6}$  K<sup>-1</sup> [6], however, the TEC through the a-axis is -1.31  $\times 10^{-6}$  K<sup>-1</sup>, for b-axis is  $5.96 \times 10^{-6}$  K<sup>-1</sup>, c-axis: -0.099  $\times 10^{-6}$  K<sup>-1</sup>. Numerous compounds characterized by layered structures, including superconductors, possess distinctive thermal expansion behaviors. Typically, these materials demonstrate pronounced anisotropic thermal expansion, wherein the bonding within the layers is robust while the bonding between layers is comparatively weak. This characteristic is exemplified in materials like graphene or graphite, where thermal expansion within the plane is minimal and can be either positive or negative, while expansion perpendicular to the plane is significantly positive [26,27]. Anisotropic thermal expansion is also evident in layered superconductors such as REFeAsO (where RE represents a rare earth element) and AEFe<sub>2</sub>As<sub>2</sub> (with AE denoting Ca, Sr, or Ba [28,29]) compounds, as well as Na<sub>x</sub>CoO<sub>2</sub> [30], MgB<sub>2</sub> [31,32], and YBaCuO<sub>7-x</sub> [33]. For instance, in the parent AEFe<sub>2</sub>As<sub>2</sub> compound, there is a discernible anisotropic thermal expansion, notably above its structural or antiferromagnetic transition, with the c-axis coefficient of thermal expansion being approximately three to four times greater than that of the a-axis [34]. One of the other examples with anisotropic expansion is  $Tm_2Fe_{17,x}Cr_x$  magnetic material [35]. For x < 2 it exhibits negative TEC through the c-axis near the Curie temperature, however, this negative expansion region changes with Cr substitution. The NTE effect may be induced in CuO nanoparticles, which was presented by Zheng et al., [36]. Interestingly, the anisotropic TEC was discovered in the nanocrystals, whereas it was not observed in the bulk counterpart. For some alloys, such as titanium-niobium, the martensitic transition may cause anisotropic structural changes. As shown by Gehring et al., the TECs through the a- and c-axis are positive for undeformed TiNb<sub>15</sub>, TiNb<sub>20</sub>, TiNb<sub>22</sub>, and TiNb<sub>24</sub>, whereas are negative for the b-axis reaching around -40  $\times$  10  $^{-6}$   $K^{-1}$  between -170  $^{\circ}C$  and 90  $^{\circ}C$  [37]. The oxide materials from A2M03O12 and AMgM03O12 exhibit a strong dependence between thermal expansion and elastic anisotropy, which was shown by Romao et al. [38]. The authors describe that AO<sub>6</sub> octahedra distortion may give contribute to anisotropic, and in effect negative TEC. A large group of MM'X, where M and M' are transition metals and X is the 13th or 14th group element, undergo a martensitic transition. In the case of the Mn<sub>0.6</sub>Fe<sub>0.4</sub>NiGe<sub>0.5</sub>Si<sub>0.5</sub>In<sub>30</sub> composite, strong anisotropic expansion was investigated and reported by Zhou et al., [39]. In this material magnetically induced changes were examined, where average TEC was around  $-32 \times 10^{-6} \text{ K}^{-1}$  when the composite sample was oriented perpendicularly and  $-59 \times 10^{-6}$  K<sup>-1</sup> when oriented parallelly to the field in the 303-336 K range. Nevertheless, according to Takenaka, large anisotropic thermal expansion behavior limits the practical applications of such materials, because of their strong dependence on their morphology [40].

## 2.3. Negative thermal expansion

One of the first scientific reports about abnormal thermal expansion was observed in ice in the middle of the 19th century [41]. The negative TEC in H<sub>2</sub>O and D<sub>2</sub>O existing in P6<sub>3</sub>/mmc space group was reported by Röttger et al., [42], where the water density was decreasing between 0 °C and 4 °C, and for ice below -198 °C, what was attributed to low-energy transverse vibrational modes (<50 cm<sup>-1</sup>) [42]. So far, the origin of negative expansion is described as the result of M-O-M transverse vibrations changing with the temperature, where the effective metal-metal distance is effectively decreasing, maintaining the bond lengths, which is schematically shown in Fig. 1b. Since transverse

vibrational modes have lower excitation energy than longitudinal modes, they are excited at lower temperatures. In general, the unnatural behavior of material shrinkage upon heating has its nature in atomic bonds. It typically involves the transverse motion of atoms or the libration of a rigid group of atoms [43]. However, the mechanism of this is still found to be complex to reveal and clearly describe. So far, the negative expansion is rather assigned to higher order mechanisms, e.g. supramolecular effects such as magnetostrictive and displacive phase transitions, low-frequency phonon modes, or ferroelectric transitions [44]. One of the other possible mechanisms of negative expansion may be so-called atomic radius contraction mechanism, which results from the difference in the atomic radius depending on the oxidation state of the respective element. Since the atomic radius depends on the oxidation state, coordination number, spin configuration, and electronic configuration. An example may be Sm<sub>2.75</sub>C<sub>60</sub> where charge transfer is thermally induced and the resulting contraction occurs when the expansion of an electron-accepting atom is relatively small and the contraction of an electron-donating atom is relatively large [45]. The phenomenon of NTEs gained significant attention in 1996 following Sleight's group's discovery of the substantial NTE exhibited by cubic ZrW<sub>2</sub>O<sub>8</sub> across a wide temperature range [46]. Since then, many NTE compounds and mechanisms have been documented. These include framework compounds driven by low-frequency phonons [47], such as Prussian blue analogs [48-50], fluorides [51,52], cyanides [53], metal-organic frameworks [54-56], oxides [46], and others. Additionally, magnetovolume effects have been observed in antiperovskite manganese nitrides [57,58], alloys [59] have shown NTE properties, intermetallic charge transfer has been implicated, ferroelectrostriction has been identified in ABO3-based materials [60], and size effects have been noted in nanoparticles [61].

Many crystal structures of NTE materials exhibit a distinctive twocoordinate  $M_1$ -O- $M_2$  linkage within cation polyhedra, forming a threedimensional lattice. These linkages are prevalent in NTE materials characterized by open-framework structures. The transverse vibration around the  $M_1$ -O- $M_2$  linkage plays a critical role in facilitating NTE within open-framework structures, as transverse vibrations are energetically more favorable than longitudinal vibrations. When the  $M_1$ - $M_2$ linkage is strong, the length of the  $M_1$ - $M_2$  bond contracts due to transverse vibrations of oxygen, while it expands under longitudinal vibrations [62–64].

Interestingly, contrary to most known metals and alloys, some alloys exhibit negative TEC, however, the temperature range may not be useful for specific technical applications. For instance,  $\alpha$ -Mn or Fe + Ni alloys have TEC lower than  $-90 \times 10^{-6}$  K<sup>-1</sup> below -240 °C [65].

Nevertheless, in cryogenic temperatures, very accurate and nonconventional measurement techniques of thermal expansion are crucial for metals and alloys. For example, using a precise three-terminal capacitance method we are able to detect spatial changes around 0.01 Å in thickness in a temperature range of 77–350 K [66]. Not only metals are known for possible negative expansion. For example various ceramic materials with open-framework structures, such as the NaZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NZP) [19] family, AM<sub>2</sub>O<sub>7</sub> (A = Hf, Zr, Ti, M = V, P), ZrW<sub>2</sub>O<sub>8</sub> [67], zeolites [68], Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> [69], metal-organic frameworks [70], Fe[Co (CN)<sub>6</sub>] [71], ScF<sub>3</sub> [72], Zr<sub>0.4</sub>Sn<sub>0.6</sub>Mo<sub>2</sub>O<sub>8</sub> [73], and exhibit NTE. Examples of observable reasons, origins, and nature of negative thermal expansion with representative materials, are schematically shown in Fig. 2a.

Another important physical property that can help to evaluate and understand the negative expansion is the so-called Grüneisen parameter, which according to numerous interpretations and formulations can be expressed as:

$$\gamma = V \left(\frac{dp}{dE}\right)_{V} = \frac{\alpha K_{T}}{C_{V}\rho} = \frac{\alpha K_{S}}{C_{p}\rho} = \frac{\alpha v_{s}^{2}}{C_{p}} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_{S}$$
(8)

Where *V* is volume, *p* is pressure, *E* is energy,  $\alpha$  is volumetric thermal expansion coefficient,  $K_T$  and  $K_p$  are bulk moduli at constant temperature and pressure respectively,  $C_V$  and  $C_p$  are heat capacities at constant volume and pressure respectively,  $v_s$  is the speed of sound in the material,  $\rho$  is density and *S* is entropy [74]. According to the Grüneisen theory, when we rewrite this equation as:

$$\frac{\alpha}{\chi} = \gamma \frac{C_V}{V} \tag{9}$$

Where  $\chi$  is isothermal compressibility, we can notice that this rule experimentally agrees for many solid materials in wide temperature ranges, where the constant parameter  $\gamma$  can express the anharmonicity of the considered material [75]. For instance, in  $\alpha$ -ZrW<sub>2</sub>O<sub>8</sub> the mode Grüneisen parameters were calculated by means of the DFT (Density Functional Theory) method within the Debye-Einstein model of quasi-harmonic approximation [76]. The results clearly show that these modes have negative mode Grüneisen parameters which contributes to negative expansion in this material. Similarly, the negative Grüneisen parameters reached almost -20 in Zn(CN)<sub>2</sub>, which was shown by Zwanziger [77]. The anharmonicities and energies of these modes significantly contribute to negative expansion in this material, especially at low temperatures.

In general, theoretical calculations are also a powerful tool for



Fig. 2. a) Observable reasons, origins, and nature of negative thermal expansion in already known systems with examples b) Number of articles connected with "negative thermal expansion" in each year, according to the Scopus database [87].

investigating negative expansion. The lattice calculations, especially lattice dynamics may provide interesting results, considerations, and discussions. According to an extensive review reported by Dove et al., [78] the potential energy well calculations may reveal the role of intrinsic anharmonic interactions in NTEs. Moreover, the DFT method allows to perform lattice dynamics calculations for many systems such as Zn(CN)<sub>2</sub>, Y<sub>2</sub>W<sub>3</sub>O<sub>12</sub>, ZrW<sub>2</sub>O<sub>8</sub>, and Cu<sub>2</sub>O. Another example is the so-called zentropy theory presented by Liu et al., where results obtained by DFT calculations show an explanation of why the volume of considered material decreases with increasing temperature [79]. The DFT method may be also useful for NTE examination using first-principle studies of phonon anharmonicity e.g. in scandium trifluorides. As shown by Oba et al., the results obtained with the Vienna ab initio Simulation Package (VASP) showed that the quartic anharmonicity is required to replicate the observed transition between positive and negative TEC with increasing temperature [80]. Moreover, the authors presented that both cubic and quartic anharmonicities are equally important for understanding the large negative expansion in ScF<sub>3</sub>. Similar considerations were performed by Jiao et al., for ferroelectric PbTiO<sub>3</sub> using DFT and VASP, focusing on Grüneisen parameters of the tetragonal phase of this material. The calculations show that the anisotropic expansion of the unit cell, where positive TEC was obtained through the a-axis, and negative TEC through the c-axis in temperatures from 0 to 900 K. Importantly, it was concluded the results match well with the experimental values. Therefore, as presented in the given examples, the theoretical calculations and considerations are complementary to experimental results and are essential to have a deeper insight into understanding the mechanisms of NTE. Recent studies based on theory and simulation have disclosed the physical mechanisms behind NTE behavior in many materials such as CaZrF<sub>6</sub> and ScF<sub>3</sub>, these studies demonstrated that the NTE behavior originates from the anharmonic nature of phonon modes with low energy, especially transverse vibrational modes related to rigid unit motions. These modes consist of quartic anharmonicity, which helps to stabilize their frequency and restrains thermal disorder at elevated temperatures. According to the analysis of the phonon density of states, these low-frequency modes (because of their high degeneracy and low energy) become gradually populated as temperature increases. This results in a notable enhancement in the amplitudes of transverse vibrational, resulting in a decrease in the average interatomic distances thereby leading to lattice contraction which characterizes the behavior of NTE [81,82]. Additionally, the molecular dynamics simulations demonstrate that along transverse directions the coordinated motion of atoms causes a steady contraction of the entire lattice. Despite the increase in thermal energy, the coordinated motion of atoms causes a reduction in the volume of material, which is crucial for NTE [83].

Most recent studies report that several novel groups of materials have emerged, exhibiting significant NTE behavior induced by transverse vibrational modes and various structural characteristics. These studies further enhance the understanding of NTE behavior in solid materials, demonstrating promising performance and tunability. For instance, Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> shows NTE behavior in the 325-375 K temperature range. The NTE behavior in Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is linked to the Jahn-Teller transition of  $\mathrm{Fe}^{2+}$  ions. This transition shifts from a static state to a dynamic state, resulting in a decrease in the average bond length and an overall contraction of the lattice [84]. The  $MHfF_6$  (M = Ca, Mn, Fe, and Co) group materials displayed isotropic and tunable NTE behavior. The study revealed that the origin of the NTE is associated with the transverse thermal vibrations of F atoms, characterized by negative Grüneisen parameters, and dominated by low-frequency phonons. The degree of expansion varies with changes in the atomic number of M atoms. As the atomic number of M atoms increases, the stiffness of M-F linkages also increases, thereby decreasing the contribution of lowfrequency transverse vibrational modes and shifting from strong NTE to moderate NTE and ultimately to near-zero thermal expansion [85]. Similarly, the cubic CaTiF<sub>6</sub> material demonstrates remarkable isotropic

NTE behavior with  $\alpha$ L of  $-7.26 \times 10^{-6}$  K<sup>-1</sup> over a temperature range between 175 and 475 K. The NTE behavior is associated with transverse thermal vibrations of F atoms, identified by density functional theory [86].

What is also important and worth mentioning, is that recently the interest of NTEs is increasing. According to the Scopus Database, the number of articles has been rapidly growing, even at an exponential rate since around 2000. The schematic graph is shown in Fig. 2b. The data was gathered using the "Article title, Abstract, Keywords" search option, and the "negative AND thermal AND expansion" phrase search option. At the beginning of this increase, mostly  $AB_2O_8$  and  $A_2W_3O_{12}$  families were investigated, however, at that time scientists were rather stating that "they will have applications in the future" [44]. After several reports regarding NTE rare-earth manganites such as  $Sm_{0.85}Zn_{0.15}MnO_{3-\delta}$  or NdMnO<sub>3</sub> which are good electronic conductors, the increased interest began resulting in 456 articles in 2023 and 494 articles in 2024 in the field of negative thermal expansion.

Different NTE materials possessing different crystal structures have different sources of negative expansion in different ranges. To give some examples, we gathered them in Table 1.

#### 3. Experimental techniques for TEC evaluation

Determining the thermal expansion coefficient of a material requires precise measurements of both displacement and temperature in programmed thermal cycles or programs defined by the user. Various experimental techniques have been developed for this purpose, ranging from absolute methods to relative techniques utilizing reference materials. These methods exhibit a wide diversity in how they measure displacement, including mechanical transmission, non-contact optical imaging, diffraction patterns, and other specialized approaches. Probably one of the most common techniques to measure and evaluate the relative elongation with temperature is dilatometry [102]. This method may be applied to almost all solid-state materials up to their melting point [103]. The extracted data allow us to determine the TEC and glassy materials' glass transition temperature for crystallization. The measured sample is placed in the furnace and is directly connected to the displacement sensor by transmission rods. The read-out electronics are connected to the computer device which registers the length and temperature changes upon previously set heating/cooling program, which is schematically shown in Fig. 3a) [103–106]. One of the other, but still a common technique to evaluate the TEC is x-ray diffraction performed as a function of temperature. Such experiments are performed at elevated temperatures, namely high-temperature X-ray diffraction, which is abbreviated to HT-XRD. However, measurements are also possible in low temperatures, e.g. for ice examination, low-temperature magnetic transitions, or single crystal examinations under cryogenic conditions [107–109]. In general, there are some differences between dilatometry and XRD studies as a function of temperature, although both methods measure the expansion. In the case of dilatometry, we measure the thermal displacement of a bulk sample, and in HT-XRD the expansion of the crystal lattice is measured. In general, the bulk expansion properties should arise from the expansion of the crystal lattice, however, it is not a general rule because of anisotropy or chemical expansion of the sample. For instance, in the case of orthorhombic  $Sm_{0.85}Zn_{0.15}MnO_{3-\delta}$  (SZM15) which exhibits bulk negative expansion, its "b" and "c" lattice constant increases as a function of temperature [110]. The authors stated that this phenomenon cannot be explained by the thermal shrinkage of the unit cell, therefore it is more complex. In some cases, when we expect a structural transition upon heating or cooling the material, very precise expansion measurements are needed. For this purpose, neutron diffraction is a suitable method as an advanced technique to accurately characterize the thermal expansion of various materials. The difference between a typical X-ray diffraction method and neutron diffraction is that for the first one, the X-rays are scattered by the electrons of atoms. In neutron diffraction, the neutrons are scattered by the nucleus.

#### Table 1

Examples of negative thermal expansion materials' parameters. \*Averaged from volumetric or anisotropic expansion coefficient. If some critical parameters are not available in the reported studies, it is indicated as N/A.

Material	Temperature range of negative expansion (K)	Unit cell volume change (%)	Crystal structure	α <sub>L</sub> (ppm/ K)*	NTE source	Ref.
Bi <sub>0.95</sub> La <sub>0.05</sub> NiO <sub>3</sub> BiNi <sub>0.6</sub> Fe <sub>0.4</sub> O <sub>3</sub>	300–370 430–500	-2.9 $\sim -2$	Triclinic Rhombohedral	-137 -77	Charge transfer transition Polar-nonpolar transition	[88] [89]
$Ca_2Ru_{0.9}Mn_{0.1}O_4$ Cd(CN) <sub>2</sub> ·CCl <sub>4</sub>	150-400 170-375	-0.8 N/A	Orthorhombic Cubic	N/A -33.5	Metal-insulator transition Transverse vibrational modes	[90] [91]
$CuMgP_2O_7$	173–303	N/A	Monoclinic	-3.34	Transverse vibrational modes	[92]
Cu <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	5-375	N/A	Monoclinic	-30.0 -9.2*	Reducing Cu—P and Cu—Cu bonds	[93]
Mn <sub>0.98</sub> CoGe	310-400	~-4	Orthorhombic	-141	Magnetic transition	[59]
Mn <sub>3</sub> Cu <sub>0.5</sub> Ge <sub>0.5</sub> N	285-315	N/A	Cubic	-65.3	Phase transition	[ <mark>94</mark> ]
Mn <sub>0.6</sub> Fe <sub>0.4</sub> NiGe <sub>0.5</sub> Si <sub>0.5</sub> In <sub>30</sub>	270-340	N/A	Hex. & ortho.	0.3*	Magnetic transition	[39]
Mn <sub>3</sub> Zn <sub>0.7</sub> Sn <sub>0.3</sub> N	299-373	N/A	Cubic	-30	Magnetic transition	[95]
Pb <sub>0.8</sub> Bi <sub>0.1</sub> Sr <sub>0.1</sub> VO <sub>3</sub>	450-700	-11.1	Tetragonal	-263	Polar-Nonpolar Transition	[ <mark>96</mark> ]
0.4PbTiO <sub>3</sub> -0.6BiFeO <sub>3</sub>	298-923	N/A	Tetragonal	-13*	Ferroelectric transition	[ <mark>97</mark> ]
Sc <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub>	0 (theoretical)	N/A	Orthorhombic	$-2^{*}$	Structural transition	[38]
Sm <sub>0.75</sub> Ce <sub>0.25</sub> S	100-260	-2.7	Cubic	-107	Charge transfer transition	[ <mark>98</mark> ]
TiNb <sub>24</sub>	273-348	N/A	Orthorhombic	~6*	Structural transition	[37]
Tm <sub>2</sub> Fe <sub>16.5</sub> Cr <sub>0.5</sub>	340-400	N/A	Hexagonal	-3.05*	Magnetic transition	[35]
$Zn_{1.6}Mg_{0.4}P_2O_7$	280-350	-0.04	Monoclinic	-60	Structural transition/ Conventional	[99]
$Zr_2S_{0.76}P_2O_{12-\delta}$	303-393	-0.3	Trigonal	$^{-10}$	Conventional	[100]
$ZrW_2O_8$	0.3-300	-1.1	Cubic	-9	Conventional	[101]



**Fig. 3.** Schematic illustration of different techniques for measuring thermal expansion coefficient and determination of TEC results of different materials: a) Schematic illustration of the principle of dilatometry technique, *Reproduced with permission* [103] *Copyright 2018, Elsevier*, b) Thermal expansion curve of SCNy (y = 0.00–0.20) using dilatometry technique, *Reproduced with permission* [138] *Copyright 2010, Elsevier*, c) Thermal expansion curves of the BSCN–xGDC mixtures using dilatometry technique, *Reproduced with permission* [115] *Copyright 2014, Elsevier*, d) Thermal expansion curves of the BSCNx oxides using dilatometry technique, *Reproduced with permission* [115] *Copyright 2014, Elsevier*, d) Thermal expansion curves of the BSCNx oxides using dilatometry technique, *Reproduced with permission* [115] *Copyright 2013, Elsevier*, e) Schematic illustration of the principle of optical interferometry technique, *Reproduced with permission* [129] *Licensed under CC BY 4.0 (http://creativecommons.org/licenses/by/4.0/)*, g) TEC result of the aluminum truss structure using Laser interferometry method, *Reproduced with permission* [129] *Licensed under CC BY 4.0 (http://creativecommons.org/licenses/by/4.0/)* h) Thermal expansion curve (the solid curve) as a function of the temperature of ZnSe using Laser interferometry, *Reproduced with permission* [135] *Copyright 2009, Elsevier*.

Moreover, X-ray scattering diminishes with the ratio of  $\sin\theta$  divided by wavelength, which is not observed for neutrons. Scattering power itself is a nuclear property hence it is weakly dependent on atomic number, which is an advantage for detecting light elements when compared with typical X-rays. Since neutron has a magnetic moment, we also observe magnetic scattering for paramagnetic ions [111]. Therefore, despite many similarities in both techniques, neutron diffraction is more precise when compared with typical X-ray diffraction. Using this technique, a tetragonal to orthorhombic phase transition was examined in SrFeAsF around -93 °C [112] by continuously collecting data every minute from 2 K to 240 K at a rate of 0.4 K/min. A similar approach was conducted for ReO<sub>3</sub>, an NTE material, by collecting diffraction data between 2 K and 300 K [113]. Brunauer et al. used this technique to investigate the mullite at temperatures up to 1600 °C [114]. Conventional techniques to calculate the material's coefficient of thermal expansion usually depend on dilatometry. Leilei et al. [115], and Zhang et al. [116] used the dilatometry technique and determined the thermal expansion of  $SrCo_{1-\gamma}Nb_{\gamma}O_{3-\delta}$  (SCNy, y = 0.00-0.20),  $Ba_{0.6}Sr_{0.4}Co_{0.9}Nb_{0.1}O_{3-\delta}$  $-Gd_{0.1}Ce_{0.9}O_{1.95}$  (BSCN-xGDC, x = 0, 10, 20, 30 and 40), and  $Ba_xSr_{1-x}Co_{0.9}Nb_{0.1}O_{3-\delta}$  (BSCNx, x = 0.0-0.8) perovskite oxide, the thermal expansion curves vs temperatures are shown in Fig. 3(b, c, d) respectively. Although, this technique can be costly because it analyses all the materials simultaneously at the same time. Alternative techniques have been developed in response to this challenge to improve costeffectiveness. Letilly et al. [117] explored at room temperature with the use of X-ray diffraction (XRD) to analyze materials. Their technique focused on analyzing the samples that have been heated at different temperatures, considering that chemical expansion during heating could affect the final TEC values of materials. Blum et al. [118] Introduced an alternative method called the standard F-design, which is based on the principle that materials uniformly expand in all directions. Like Letilly et al.'s technique, this approach merges the fundamental ideas of linear expansion evaluated at room temperature after high-temperature sintering with accurate micrometer readings. Overall, this approach offers a more economical and potentially simpler alternative for calculating thermal expansion properties.

Generally, high-temperature (HT) XRD is the most common, economical, and precise technique researchers use to determine the TEC of materials. The HT-XRD advantage over the dilatometry technique is that dilatometry needs external physical dimensions (width, length, and volume) while the HT-XRD measures crystal lattice changes directly without external physical dimensions. The HT-XRD precisely delivers the lattice parameters as a function of temperature. From the diffraction angle, the interplanar spacing (d) is calculated using Bragg's law, while the lattice parameter ( $\alpha$ ) is calculated from the specific crystallographic plane. During HT-XRD measurements, the material is heated from room temperature to high temperature, and the lattice parameter changes are recorded precisely. The TEC of the material is determined from the temperature-dependent lattice parameter. Edwards et al. [119] used HT-XRD and studied the thermal expansion of Molybdenum, Tantalum, Niobium, and Platinum. Yasumasa et al. [120] determined precisely the thermal expansion coefficient and lattice parameter of silicon using HT-XRD. Fiquet et al. [121] determined the thermal expansion of periclase (MgO), spinel (MgAl<sub>2</sub>O<sub>4</sub>), lime (CaO), and corundum (Al<sub>2</sub>O<sub>3</sub>) through HT-XRD.

Another highly effective technique to precisely measure the TEC is Optical interferometry, which utilizes the interaction of light waves and can even measure the smallest change in the dimension of the materials [66]. Therefore, it acts as an essential tool for calculating thermal expansion coefficients by offering precise and non-invasive measurements of dimensional changes in numerous materials under varying thermal conditions. Laser interferometry represents a significant advancement over traditional optical interferometry by harnessing the precision of laser beams. This technique offers unparalleled accuracy in measuring minute changes in the length of a sample. The process involves splitting a laser beam into two paths: one travels directly to a detector, while the other traverses through the sample under investigation. The schematic of the operation is shown in Fig. 3e. Upon recombining, these beams generate an interference pattern. Through meticulous analysis of this pattern, scientists can precisely quantify the extent to which the sample has expanded or contracted, thereby revealing its thermal expansion coefficient). Laser interferometry excels in studying dynamic processes characterized by rapid changes, as well as materials necessitating high-temperature testing [122]. This upgraded method provides unparalleled accuracy in detecting and measuring small variations in a material's length [123]. Employing techniques such as Michelson interferometry [124] and Electronic Speckle Pattern Interferometry [125], the principle of such techniques is based on the splitting of a laser beam into two different paths (Fig. 3f) [125]. Among the split two paths, one path passes through the material being analyzed while the other path travels toward a detector directly. At the point of recombination, the split beams combine and generate an interference pattern consisting of a series of dark and bright fringes resulting from destructive and constructive interference of the light waves. The scientists carefully analyze these fringes and precisely measure the degree of contraction or expansion in the materials, thereby enabling the determination of the TEC of that material. This non-contact technique offers exceptional sensitivity, making it suitable for a diverse range of materials and temperature conditions, from high-temperature ceramics to frangible thin films. Lucki et al. [126] used the optical interferometry technique and measured the thermal expansion coefficient of a copper rod, which is 17.4  $\text{K}^{-1} \times 10^{-6}$  well matched with the literature value of 16.9  $\text{K}^{-1} \times 10^{-6}$  [127]. Scholl et al. [124] accurately measured the thermal expansion coefficient of copper (17.3  $\pm$  0.3)x10  $^{-6}$   $^{\circ}C^{-1}$  using the optical interferometry technique and the obtained results well matched with the expected value of  $17 \times 10^{-6} \circ C^{-1}$  [127]. Jose Francisco et al. [128] applied the optical interferometry technique and studied the thermal expansion of transparent materials. Their approach demonstrated effectiveness for both liquid and solid materials such as acetone, ethanol, silica, etc.

Weipeng et al. [129] applied a laser interferometric technique and calculated the dual-material lattice's thermal expansion. The average value of the calculated thermal expansion which is  $22.99 \pm 0.54 \times 10^{-6}$  $K^{-1}$  (Fig. 3g)), matched with the literature value of (23.1  $\times$  10<sup>-6</sup>  $K^{-1}$ ) very closely [130]. The obtained results proved that this method bypasses measurement inaccuracies ascribed to translation and has the ability to eradicate errors produced by rotation. This technique amplifies accuracy and anti-interference capabilities, which makes this technique useful particularly for the measurement of thermal expansion in dualmaterial lattice structures with high precision. Pirgon et al. [131] used the laser interferometric technique and studied the thermal expansion of Carbon-fibre composites at elevated temperatures. They found that the value of thermal expansion of Carbon-fibre composites varies with both the orientation of the carbon fibers and the temperature. The calculated thermal expansion coefficient of Carbon fibers is  $-9.1 \times 10^{-7}$  K<sup>-1</sup> at room temperature. Masuda et al. [132] studied the thermal expansion of corundum (single-crystal Al<sub>2</sub>O<sub>3</sub>) using the differential laserinterferometry method, and the calculated data of thermal expansion was well aligned with the data of Watchman et al. [133] and White et al. [134] reported in the literature. Ching-Hua et al. [135] applied laser interferometry and investigated the thermal expansion of ZnSe from the 17 °C to 1080 °C temperature range. They precisely calculated the dimensional changes with temperature and determined the CTE of ZnSe as shown in (Fig. 3h). The calculated thermal expansion coefficient value for ZnSe is  $4.95 \times 10^{-6}$  °C<sup>-1</sup> at 17 and 1080 °C. They precisely calculated the dimensional changes with temperature and determined the CTE of ZnSe (Fig. 3h). There is also another technique, a confocal Fabry-Perot interferometric dilatometer arrangement utilizing single frequency helium-neon laser can be used for materials examination exhibiting very small TEC ranging between  $10^{-6}$  K<sup>-1</sup> to  $10^{-8}$  K<sup>-1</sup>. For organic thin films such as polyimide or poly(amic acid), the lateral expansion was measured with the Fizeau interference method based on

thermal stress measurements [136]. A similar approach was applied by Aurora et al., utilizing a Jamin interferometer for measuring the expansion of highly reactive fluorides [137].

There are a lot of other specialized methods that are used to measure the thermal expansion coefficient. These methods include atomic force microscopy, specific heat capacity calculations, electrical pulse heating, and thermomechanical systems. Each method provides a distinct capability, such as exceptional compatibility or sensitivity with the measurements of thin film. However, some factors for example material compatibility and temperature range must be carefully considered when choosing the appropriate method for the evaluating TEC of a material.

In the last decade, Raman spectroscopy has been illustrated as a novel and versatile tool for determining the TEC of 2D materials based on the facts that Raman bands are sensitive to strain (and stress) and temperature, and it can measure directly the frequency shift of phonon due to the strain field's perturbation induced by thermal expansion [139,140]. The principle of Raman spectroscopy is it utilizes the material vibration modes which are temperature-dependent. When the temperature changes, the lattice in the material contracts or expands resulting in changing the interatomic distances, causing shifts in the frequencies of Raman active phonons. The scientists carefully observe these shifts and relate them to temperature, using the Grüneisen parameter (links lattice changes to phonon frequency), and determine the TEC of the materials (Fig. 4a) [141].

Duhee et al. [139] used Raman spectroscopy and determined the TEC of single-layer graphene (SLG) from a temperature range of 200 to 400 K. They found that the SLG remained negative in the whole range of the studied temperature. From their study, it is concluded that when analyzing the data measurement from low-temperature transport, the strain effect arising from the TEC mismatch between the substrate and SLG must be taken into account and assumed the Grüneisen parameter  $(\gamma)$  to vary by 20 % per 100 K. The calculated TEC of SLG (Fig. 4b) is well fit between the previously theoretical estimation by (Mounet et al. [142]) and experimental data by (Bao et al. [143]). The calculated TEC of SLG is  $(-8.0 \pm 0.7) \times 10^{-6}$  K<sup>-1</sup> at room temperature. Zhongtao et al. [144] determined the TECs of different numbers of layers (2–6-layer) of MoS<sub>2</sub> after eradicating the subtract effect from 77 to 557 K temperatures range using the Raman spectroscopy technique. Below 175 K temperature, MoS<sub>2</sub> demonstrated a negative thermal expansion coefficient, highlighting its unique thermal behavior. From the 150-450 K temperature range, the MoS<sub>2</sub>'s TEC layers exhibit similar expansion trends for all different numbers of layers (Fig. 4c). The calculated TEC of MoS<sub>2</sub> with this approach is  $0.5 \times 10^{-6}$  K<sup>-1</sup>, the order of magnitude of TEC is matching with the literature [145], suggesting that Raman spectroscopy is an effective and reliable technique for investigating the MoS<sub>2</sub>'s TEC. Zhang et al. [141] used Raman spectroscopy to investigate the three-



**Fig. 4.** a) Schematic illustration of the principle of Raman spectroscopy, *Reproduced with permission* [152] *Copyright 2013, American Chemical Society*, b) Calculation of thermal expansion coefficient (Solid curve) of SLG using Raman spectroscopy, well fit between the previously theoretical estimation by (Mounet et al. [142]) and experimental data (Bao et al. [143]), *Reproduced with permission* [139] *Copyright 2011, American Chemical Society*, c) Determination of the TECs of different numbers of layers of MoS<sub>2</sub> using Raman spectroscopy. The Magnified view of the TECs is shown by the inset figure in the temperature range of 75–150 K, *Reproduced with permission* [144] *Licensed under CC BY 4.0* (https://creativecommons.org/licenses/by/4.0/) d) Schematics illustration of the three-substrate method for TEC calculation of monolayer MoS<sub>2</sub> flakes, using Raman spectroscopy, *Reproduced with permission* [152] *Copyright 2013, American Chemical Society*, e) Calculation of the TEC of MoS<sub>2</sub> by combining finite element simulations and Raman spectroscopy, *Reproduced with permission* [153] *Licensed under CC BY 4.0* (https://creativecommons.org/licenses/by/4.0/), f) Theoretical (yellow line) and experimentally calculated (red triangle) TEC of GDY using Raman spectroscopy, *Reproduced with permission* [148] *Copyright 2023, Elsevier*, g) TEC calculation of SLG (black scatter) using Raman spectroscopy, theoretical TEC calculations of SLG (green solid line) and graphite (pink solid line) by Mounet et al. [142] and SLG (orange solid line) by Sevik et al. [150]), experimental TEC calculation of SLG (blue dashed line) by Duhee et al. [149] and (red dashed line) by Shibing et al. [151]),

substrate method and determined the TEC of monolayer MoS<sub>2</sub> flakes. Their experiment used pure copper, holey, and fused silica substrates (Fig. 4d). The in-plane TEC of the MoS<sub>2</sub> monolayer was calculated from temperature dependence Raman peak shift based on lattice symmetries, analyzed by three different substrate conditions. The measured TECs in this study are in good agreement with first principle calculations previously reported in the literature. Yang et al. [146] applied a feasible method by combining numerical simulations and Raman spectroscopy and investigated the TEC of monolayer MoS2 in the 77 to 557 K temperature range. They considered and calculated the TEC mismatch between the substrate and MoS<sub>2</sub> by applying finite element simulations. The TEC of MoS<sub>2</sub> (Fig. 4e) was calculated using a numerical inversion method to match the experimental results to the simulation results. This approach is adaptable and reasonable to calculate the TEC of MoS<sub>2</sub> as well as the TEC of two-dimensional materials. Deng et al. [147] have determined the coefficient of thermal expansion of single-walled carbon nanotubes (SWCNTs) and double-walled carbon nanotubes (DWCNTs) using Raman spectroscopy, both SWCNTs and DWCNTs show positive thermal expansion of  $2 \times 10^{-5}$  K<sup>-1</sup>. At room temperature, both SWCNTs and DWCNTs demonstrated positive thermal expansion. With the addition of the inner wall nanotubes, the coefficient of thermal expansion of SWCNTs remained virtually unchanged. The approach used in this study could also be used to determine both glass transition temperature and coefficient of thermal expansion of the matrix polymers and might be extended to calculate the thermal behavior of graphene and graphene oxide. Kong et al. [148] have explored and investigated the thermal expansion behavior of graphdiyne (GDY) using density functional theory calculations and Raman spectroscopy. The calculated TEC of GDY is  $-7.18 \times 10^{-6} \text{ K}^{-1}$  at room temperature. The TEC calculation of GDY film with SiO<sub>2</sub>/Si substrate was investigated in the 180-420K temperature range and the calculated TEC of GDY well matched with the results of density functional theory calculations (Fig. 4f). The study found that the GDY has a negative thermal expansion coefficient in the 180-420K temperature range Lingling et al. [149] conducted a comprehensive Raman spectroscopy study of graphene and extracted the thermal expansion coefficient of single-layer graphene (SLG). The graphene demonstrated a negative thermal expansion coefficient in the 303–503 K temperature range without transition to positive. The calculated results are much closer to the theoretical work of (Mounet et al. [142] and Sevik et al. [150]) than the experimental work of (Duhee et al. [139] and Shibing et al. [151]) (Fig. 4g). This study gives a more precise way to calculate the TEC using Raman spectroscopy of two-dimensional materials. Overall, it can be concluded that Raman spectroscopy is a feasible alternative approach to determining the TEC of 2D materials.

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# 4. Applications of negative thermal expansion materials in ferroelectrics, magnetics, and others

Early discovered materials with negative thermal expansion, like water between 0 and 4 °C [42], were rather explored to investigate the nature of this phenomenon, i.e. bonding and the structure. However recently, the size-related effects allowed to find many applications that can be applied in different devices, where magnetic- or electric-induced structural transitions play a crucial role. After many years of experiments, scientists learned how to use this extraordinary property, and found many applications in many branches of science, giving a vast number of possibilities. Examples of usage are schematically shown in Fig. 5.

In the case of niobate ceramics such as  $AlNb_9O_{24}$ ,  $Nb_{14}W_3O_{44}$ ,  $GeNb_{18}O_{47}$ , or similar compounds, the final annealing temperature results in unique microstructure where grains are grown in preferred orientation through the axis with negative expansion. In effect, the obtained materials exhibit high strength and durability and, therefore may be applied in four-way filters for mitigating hydrocarbon CO and  $NO_x$ 



Fig. 5. Examples of negative thermal expansion materials applications.

from diesel exhaust [154]. Morelock et al. showed strong isotropic negative expansion in  $Sc_{1-x}Ti_xF_3$  solid solutions between 100 K and 500 K as an effect of cubic to rhombohedral phase transition upon cooling [155], which is schematically shown in Fig. 6a. Interestingly, the effect is observed in a wide range of substitutions.

NTE materials may also be utilized in optical applications. Recently, Liao et al., have shown Sc<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>:Yb/Er phosphors [156] with twodimensional negative TEC, i.e. -8.62  $\times$   $10^{-6}~\text{K}^{-1}$  along a-axis and  $-6.35 \times 10^{-6} \text{ K}^{-1}$  along c-axis. In this case, RE-RE distances play a crucial role resulting in lattice shrinking with increasing temperature caused by distortion of local symmetry. The results showed that lattice contraction increases the photoluminescence due to trapped and excited  $Yb^{3+}$  cations. Jin et al. presented  $Yb_{2-x}W_3O_{12}$  doped with Ho phosphors with enhanced up-conversion luminescence [157]. The authors state that the efficiency of energy transfer may be improved due to shortening the distance between sensitizers and activators caused by lattice shrinking at high temperatures. Moreover, due to the lattice contraction, namely the Ho-Yb distances decreased, the structural rigidity increased the thermal stability of the fluorescent material was greatly enhanced. Similar mechanisms were also observed in Y2M03O12, Cs3GdGe3O9, ZrScMo<sub>2</sub>VO<sub>12</sub>, HfScW<sub>2</sub>PO<sub>12</sub>, and many others [158].

Negative thermal expansion coefficients were also discovered in ferroelectric materials. One of the examples may be PbTiO<sub>3</sub> substituted by lanthanum in A-site, where the TEC in the tetragonal phase varies from -19.9  $\times$  10<sup>-6</sup> K<sup>-1</sup> in undoped material, to -1.1  $\times$  10<sup>-6</sup> K<sup>-1</sup> for Pb<sub>0.8</sub>La<sub>0.2</sub>TiO<sub>3</sub> [159]. In higher temperatures, after the structural transition to the cubic phase, the TEC rapidly grows and exceeds  $35 \times 10^{-6}$  $K^{-1}$ . In general, these lead-titanates due to their known dielectric, piezoelectric, electrooptic, and pyroelectric properties are widely used in electronics and microelectronics. Another example is Pb<sub>1-x</sub>Bi<sub>x</sub>TiO<sub>3</sub> presented by Hu et al., where also negative TEC was recorded in a tetragonal structure [160]. However, the authors observed that bismuth addition enhanced the spontaneous polarization and decreased the tetragonality weakening the negative expansion effect. The negative expansion was also observed in Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystals in the ferroelastic phase in temperatures slightly above 30  $^\circ \mathrm{C}$  and below the transition to the paraelectric phase around 70  $^\circ C$  [161]. This interesting effect occurs as a result of 632 nm light probing causing an electro-optic effect on the surface due to spontaneous polarization near the ferroelectricparaelectric phase transition.

Magnetic materials are also an object of interest in terms of negative expansion. Different types of magnetic transitions are responsible for lattice contraction, ferromagnetic to paramagnetic, anti-ferromagnetic to paramagnetic, ferrimagnetic to paramagnetic, ferromagnetic to anti-ferromagnetic, ferromagnetic to ferromagnetic, or short-range



**Fig. 6.** Different sources of negative thermal expansion in magnetic materials: a) structural transition. *Reproduced with permission* [155]. *Copyright 2014. American Chemical Society* b) cubic structure with specific magnetic spin structure  $\Gamma^{5g}$ . *Reproduced with permission* [162]. *Copyright 2021. Elsevier* c) PM spin structure. *Reproduced with permission* [162]. *Copyright 2021. Elsevier* d) internal pressure caused by (Cr/Te)-Sn bonds, giving an NTE window of operation shown in e), *Reproduced with permission* [166], *Copyright 2020. American Chemical Society* f) FM-AFM magnetic phase coexistence, *Reproduced with permission* [168], *Copyright 2019. American Chemical Society* g) external magnetic field, *Reproduced with permission* [169], *Copyright 2020. American Chemical Society* g) external magnetic field, *Reproduced with permission* [169], *Copyright 2020. American Chemical Society* g) external magnetic field, *Reproduced with permission* [169], *Copyright 2020. American Chemical Society* g) external magnetic field, *Reproduced with permission* [169], *Copyright 2020. American Chemical Society* g) external magnetic field, *Reproduced with permission* [169], *Copyright 2020. American Chemical Society* g) external magnetic field, *Reproduced with permission* [169], *Copyright 2020. American Chemical Society*.

magnetic ordering. As an example, Mn<sub>3</sub>Cu<sub>1-x</sub>Ge<sub>x</sub>N or Mn<sub>3</sub>Cu<sub>1-x</sub>Sn<sub>x</sub>N NTE alloys exhibiting antiperovskite structure can be given [162]. In this case, for the NTE phenomenon, large spontaneous magnetostriction, cubic structure with  $\Gamma^{5g}$  spin structure, and a high amount of "d" electrons are needed. A linear decrease in spatial length was observed for  $0.7 \leq x \leq 0.$  Similar behavior was also observed in  $Ag_{1-x}NMn_{3+x}$  nitride, also connected with  $\Gamma^{5g}$  ferromagnetic – antiferromagnetic transitions [163] which is shown in Fig. 6b,c. Interestingly, Lin et al., revealed that similar magnetic transitions in GaNMn<sub>3</sub> and GaN<sub>0.9</sub>Mn<sub>3</sub> nitrides may be tuned by the ball milling time of precursors [164]. It was shown that the NTE range increased from 8 °C for non-milled precursors, to 103 °C for 35 h ball-milled precursors in GaNMn<sub>3</sub>, with the TEC around  $-30 \times 10^{-6}$  $K^{-1}$ . Magnetocaloric compounds based on LaFe<sub>13-x</sub>Si<sub>x</sub> gained attention due to a broad NTE range exceeding 100 °C including room temperature [165]. In LaFe<sub>10.5</sub>Co<sub>1.0</sub>Si<sub>1.5</sub> a negative TEC of  $-26.1 \times 10^{-6} \text{ K}^{-1}$  was achieved between 240 and 350 K giving a 110 °C operation window for applications. A large NTE in a wide temperature range was obtained in magnetoelastic  $CrTe_{1-x}Se_x$  for  $0 \le x \le 0.15$  [166]. Depending on selenium content the effective negative expansion increased from 60 °C in an undoped sample, to 100 °C for CrTe<sub>0.85</sub>Se<sub>0.15</sub>. The changes in unit cell volumes along with the magnetic diagram with the NTE window are shown in Fig. 6d, e. An extended window of negative expansion was presented by Song et al., for  $Hf_{1-x}Nb_xFe_2$  alloys [167]. For the minimum niobium content, the NTE region spans between 323 K and 398 K giving a 75 K range, and for x = 0.15, it extended to 150 K where negative TEC of -8.28  $\times$  10  $^{-6}$   $K^{-1}$  was recorded in 173–323 K range. The authors reported that Fe-Fe bond lengths decreased by niobium substitution, which weakened the exchange interaction, therefore the material absorbs less thermal energy to break magnetic ordering, therefore the lattice shrinks giving a negative TEC. Another example of NTE was recently shown by Qiao et al. for Hf<sub>0.6</sub>Ti<sub>0.4</sub>Fe<sub>2</sub> alloy [168] in a wide

temperature range. What is interesting, both end members, i.e. HfFe<sub>2</sub> and TiFe2 exhibit positive TEC. Therefore, it is evident that only ferromagnetic and antiferromagnetic phase coexistence is responsible for negative expansion. What is more, the structural XRD refinements show that the volume of these phases increases as a function of temperature, however, the average unit cell volume along with linear expansion decreases in the temperature ranges between around 100 K and 300 K, what is schematically shown in Fig. 6f. Not only structural transitions or deviations may give a contribution to negative expansion. An interesting result was reported by Song et al., for the LaFe<sub>11.5</sub>Al<sub>1.5</sub> compound where contrary to the abovementioned examples, the authors show fielddriven strong NTE in an external magnetic field equal to H = 3 Twhich is probably caused by long-range magnetic ordering and spinrotation from an AFM component with a small lattice to a FM component one with a large lattice [169], what is schematically shown in Fig. 6g.

#### 5. Other applications

Not only electric and magnetic materials involve negative expansion. There are also many applications in mechanics, biology, chemistry, or even household applications in everyday life. Although it is not an object of this study, we also briefly describe them, to stress, that NTE materials find usage ability in almost every branch of science. There is an interesting group of mechanic materials called auxetic materials, exhibiting negative Poisson's ratio, which means that elongation in one direction causes elongation in the other direction, contrary to standard materials, where elongation in one direction causes compression in the other. Therefore, for such materials, negative expansion is caused not by temperature changes but by mechanical changes. According to Cabras et al., the effective TEC in auxetic materials can be described as:

$$\alpha_{E} = \frac{(1 - \eta cos^{2}\gamma)}{sin^{2}\gamma} \alpha_{c} \ (8)$$

Where  $\eta$  is a ratio of high and low TECs present in the material,  $\gamma$  is a specific angle describing the microstructure [170]. Therefore, for  $\eta > 1/$  $\cos^2\gamma$  the TEC is negative, which can be achieved in the so-called Mechanical-Auxetic Thermal-Shrinking (MATS) medium, presented by the authors, where the calculated TEC was equal to  $-2162 \times 10^{-6} \text{ K}^{-1}$ , what is schematically shown in Fig. 7a. Such huge negative TEC in MATS results both from mechanic properties (negative Poisson ratio) and thermal properties directly related to NTE. What is more, many biological applications have been extensively reviewed by Dubey et al., [171]. According to the article, NTE materials can be used in dental applications. In general, our teeth everyday experience many thermal shocks, during breakfast or other meals, and when drinking hot beverages like tea or coffee. After each sip, our tooth enamel needs to resist temperature changes around 60 °C in a few seconds. Therefore, dental implants should exhibit near zero TEC to not damage the inner/outer parts of the tooth. The idea of NTE application is to adjust and perfectly match each of the dental implant parts, i.e. crown, abutment, and the bottom core part, which is shown in Fig. 7b. Such a solution has many advantages, since for dental applications, specific electric or magnetic properties are not important, therefore many NTEs may be used, however, in these applications' excellent biocompatibility along with osseointegration is crucial. Also in chemistry, NTE materials can be useful. As presented by Shen et al., mechanoresponsive polymers can be applied in drug delivery systems, where the TEC of polyacrylamide film containing s-dibenzocyclooctadiene, is extraordinarily low, around  $-1200 \times 10^{-6} \text{ K}^{-1}$  [172], which is shown in Fig. 7c. Although, the temperature range where negative TEC exists is relatively narrow, i.e. between 17 °C and 42 °C, it is still acceptable in terms of the human body and drug delivery systems. What is more, negative or zero-expansion materials find application in our households in everyday life [173]. Low-expansion glass ceramics were an object of interest many years ago, because of the industrial problem of manufacturing tableware, to find a compromise between customers' needs and material processing [174]. Cooking hobs are also interesting examples, because of their irregular thermal expansion [175]. According to Hanson and Fernie, materials exhibiting the TEC lower than  $5 \times 10^{-7}$  K<sup>-1</sup> can effectively withstand large temperature differences and therefore may be applied as cooking hobs [176]. To find a proper material, simulation techniques such as computational fluid dynamics allowed to predict the thermal behavior of a cooking hob [177]. Moreover, in the car industry, there are also NTE

applications. For instance, the expansion of catalytic converters needs to be properly selected, since substrate and steel shell exhibit different TECs [178]. The computer simulations show that it can be adjusted using specially designed materials with improved durability [179]. For example, a thin-wall substrate exhibits lower negative TEC when compared to a typical ceramic substrate used in such applications [180]. An interesting group of multicomponent composites was recently reported by Yuan et al., and Lu et al., respectively for  $Mn_{3(1-x)}Cu_{0.5}Ge_{0.5}N$  (for x = 0.1, 0.2, 0.3) and  $Mn_3Ga_{1-x}Ge_xN$  [94,181]. These antiperovskites exhibit negative TECs in a relatively wide temperature range, which enables to use of them in aerospace applications.

# 6. Recent advances in negative thermal expansion materials for solid oxide cells

Despite the vast number of applications of negative thermal expansion materials in different branches of science, probably, the most rapidly growing interest is the electrochemical branch involving SOFCs and SOECs. According to the data presented by the International Energy Agency [182], total global electricity consumption is rapidly growing, even faster than expected. Therefore, scientists are looking for new sources of clean, cheap, and efficient energy that can be delivered by SOFC. However, one of the most common problems that limit the commercial usage of Solid Oxide Cells (SOCs) is the thermal mismatch between the electrolyte and the electrode. The TEC for typical electrolytes, like LSGM or YSZ is around  $10 \times 10^{-6}$  1/K [183–185] and for cathodes, it could be around 30  $\times$  10  $^{6}$  1/K [186]. Therefore, in extreme cases, the difference may be even up to a few hundred percent, which is extremely harmful to the device and may damage the cathode layer. Additional strain may occur which leads to cracks and layer delamination. In effect, the overall performance of the SOCs is rapidly decreasing. To overcome these TEC mismatch problems, some solutions have already been introduced. One of the ideas is to add some electrolyte, e.g. YSZ or GDC, to the cathode during the synthesis to obtain a composite cathode with lowered TEC [187,188]. The authors did not observe the cathode layer delamination. On the other hand, the total conductivity is lowered by electrolyte addition [187,189]. The other idea is to reduce the amount of cobalt, which is responsible for relatively high TEC. For instance, the TEC can be lowered from 21.5  $\times$  10  $^{6}$  1/K [190] in  $\mbox{PrBaCo}_2\mbox{O}_{5+\delta}$  to  $17.2\times10^{-6}$  1/K [191] by completely replacing Co with Fe. Still, the TEC is not relatively close to the electrolyte, and much research has been done to adjust it properly. Therefore, recently the idea of utilization of NTEs in SOCs appeared as a possible solution for TEC



Fig. 7. Other examples of NTE applications: a) in mechanics, as auxetic materials. Reproduced with permission [170]. Copyright 2019. Royal Society Publishing b) in biology, as dental implants, and c) in chemistry, as drug delivery systems. Reproduced with permission [172] Copyright 2013. Springer Nature.

mismatch between a cathode and an electrolyte. These materials allow for adjustment of the expansion, and in principle, to have near-zero TEC difference. It could be possibly done by adding different amounts of a certain NTE to previously obtained cathode material. The thermal offset proposed by Zhang et al., [192] was performed by adding  $Y_2W_3O_{12}$  NTE oxide exhibiting TEC around  $-7 \times 10^{-6}$  K<sup>-1</sup> to Y-doped SrNb<sub>0.1</sub>Co<sub>0.9</sub>O<sub>3-6</sub> cathode. The obtained composite cathode with NTE addition has the TEC of  $12.9 \times 10^{-6}$  1/K allowing it to obtain a superior power density of 1.69 W·cm<sup>-2</sup> at 750 °C.

One of the most common perovskite materials, with good electrochemical properties, is A-site doped samarium-based manganate possessing orthorhombic perovskite structure with the chemical formula Sm<sub>1-x</sub>A<sub>x</sub>MnO<sub>3-δ</sub>. For instance, Jia et al. presented a composite cathode, where the  $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.1}Ti_{0.1}O_{3-\delta}$  acts as an electrocatalytically active component, and Sm<sub>0.85</sub>Zn<sub>0.15</sub>MnO<sub>3-δ</sub> (SZM) was an NTE material which exhibits the TEC of -7.01·10<sup>-6</sup> 1/K between 400 °C to 750 °C [193]. The authors synthesized four single cells with different SZM content ranging from 0 to 30 % with a composition of NiO–BZCY|SDC| BSFCT-xSZM. The 30 wt% addition of SZM material slightly lowered the maximum conductivity from around 18 S·cm<sup>-1</sup> to around 10 S·cm<sup>-1</sup>, simultaneously lowering the TEC from 37.9.10<sup>-6</sup> 1/K to 18.0.10<sup>-6</sup> 1/K (Fig. 8a), which is more than 50 %. For the best composition, i.e. with 20 wt% addition of SZM, the peak power density increased from 559 mW/cm<sup>2</sup> to 918 mW/cm<sup>2</sup> at 750 °C giving around 60 % increase when compared to undoped pristine cathode (Fig. 8b). Therefore, the performed optimizations allowed to greatly improve the electrochemical performance of single cells.

The application of SZM material was also considered by Liu et al., [194] where the authors optimized the NTE addition to the

 $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$  cathode. Interestingly, the maximum total conductivity decreased from around 1100 S·cm<sup>-1</sup> to around 180 S·cm<sup>-1</sup> with the addition of 30 wt% of SZM. Despite this fact, the overall performance of the single cells based on NiO-SDC|SDC|PBSC-xSZM was better for composite cathode with NTE addition. What is more, to prove the thermomechanical stability, the authors performed several thermal treatments of the best single cell, i.e. rapid heating and cooling from 450 °C to 600 °C. The presented results show that the peak power density of the cell with the cathode prepared with the NTE addition decreased visibly after 20 h, which is shown in Fig. 8c.

Another SZM application was demonstrated by Hu et al., [195] as an additive to SrNb<sub>0.1</sub>Co<sub>0.9</sub>O<sub>3.6</sub> cathode. The authors synthesized different composite cathodes by adding 10 to 30 wt% of the NTE. This allowed to reduce the TEC of the composites from around  $26 \times 10^{-6}$  1/K to  $14 \times 10^{-6}$  1/K. Similar to experiments performed by Jia [193], the total conductivity was slightly lowered by adding the SZM. All in all, the performance of the single cell was visibly higher when compared to the pristine cell without NTE, e.g. at 700 °C the recorded PPD respectively was 1.22 W·cm<sup>-2</sup> and 0.8 W·cm<sup>-2</sup>. What is more, at a constant current density of 0.8 A·cm<sup>-2</sup> because of the degradation possibly caused by TEC mismatch between electrode and electrolyte, the voltage in a single cell without NTE had a degradation rate of around 0.06 %/h, whereas the sell with SZM material exhibits lower degradation rate of around 0.03 %/h (Fig. 8d).

Also, other A-site doping in orthorhombic samarium manganate was recently examined to check the NTE properties. Li et al., synthesized Sm<sub>1-x</sub>Cu<sub>x</sub>MnO<sub>3-\delta</sub> where  $x \leq 0.2$  [196], however, the negative TEC occurs only for higher copper content, with a minimum of -5.93  $\times$  10<sup>-6</sup> 1/K between 200 °C – 600 °C for Sm\_{0.85}Cu\_{0.15}MnO\_{3-\delta}. Another perovskite



Fig. 8. NTE materials applications in Solid Oxide Cells. a) TEC adjusting in BSCFT cathode using SZM15 NTE material, *Reproduced with permission* [193], *Copyright 2022. IOP Publishing* c) PPD of NiO-SDC|SDC|PBSC-xSZM cell after thermal cycling, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [194], *Copyright 2022. IOP Publishing* d) stability of SNC-xSZM|GDC|YSZ|NiO-YSZ single cells at 700 °C, *Reproduced with permission* [198], *Copyright 2022. Elsevier* f) EDX mapping showing the uniform distribution of elements in the composite cathode with NTE material, *Reproduced with permission* [202], *Copyright 2024. Elsevier* g) schematic representation of advantageous constant power output in the single symmetrical cell, *Reproduced with permission* [204], *Copyright 2024. Elsevier*.

with negative thermal expansion was reported by Hirano et al. in Gd<sub>1</sub>.  $_xSr_xMnO_{3-\delta}$  [197]. Both abovementioned materials, i.e. Cu-doped SmMnO<sub>3</sub> and Sr-doped GdMnO<sub>3</sub> may be applied as an NTE additive to a cathode material in SOC, however, such studies have not been performed yet. In these manganates, it is believed that a-axis negative expansion is caused by Mn<sup>3+</sup> Jahn-Teller ion.

Another example of NTE utilization was recently shown by Wang et al., where NdMnO<sub>3</sub> was chosen as NTE material and NdBaCo<sub>2</sub>O<sub>5+δ</sub> double perovskite was chosen as a cathode in reversible SOCs [198]. The effect of the 50 wt% addition of NdMnO<sub>3</sub> allowed to ideally match the electrolyte/electrode interface TEC, which greatly improved the overall cell performance. For example, after 25 cycles at 750 °C under charge  $\pm 200 \text{ mA} \cdot \text{cm}^2$ , the cell still exhibited stable and reversible performance. The DRT analysis showed that the peaks attributed to the oxygen surface exchange, ion transport, and electron transfer did not change significantly, proving very good durability and thermal cycling resistance, which additionally was presented on cross-section SEM images (Fig. 8e). The drawn conclusion by the authors was that their composite cathode with the NdMnO<sub>3</sub> addition is potentially a very good electrode material for reversible SOCs due to their good OER and ORR activities.

The addition of NdMnO<sub>3</sub> was also investigated by Lu et al., [199] to barium strontium ferrite Ba<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3- $\delta$ </sub>. Contrary to the previous abovementioned examples, the authors considered a proton-conducting SOFC with BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3- $\delta$ </sub> electrolyte. The addition of the NTE phase did not change the total conductivity significantly, while greatly improving the performance of the cell. For instance, the peak power density increased by 90 % at 500 °C and by 42 % at 750 °C. The polarization resistance decreased from 7.272  $\Omega$ ·cm<sup>2</sup> to 3.319  $\Omega$ ·cm<sup>2</sup> at 500 °C, and from 0.12  $\Omega$ ·cm<sup>2</sup> to 0.054 at 750 °C.

The idea of NTE utilization also was proposed by Sun et al., in protonic ceramic fuel cells [200]. The authors prepared the  $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$  (BSF) nanofibers which were heated at different temperatures and were a main component of the composite cathode. The NdMnO<sub>3</sub> NTE oxide was used as an additive to BSF in a mass proportion 7:3. The obtained composite cathode was used to prepare Ni-BZCY| BZCY|BSF-30NM single cell. At 700 °C the achieved power density was 1.17 W/cm<sup>2</sup>, and the polarization resistance was 37 m $\Omega$ ·cm<sup>2</sup>.

Recent advances were reported using SZM15 material as an addition to a  $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$  (PBSCF) double perovskite cathode [201]. The authors prepared several single anode-supported cells with the composition of NiO-YSZ|YSZ|GDC|PBSCF-xSZM, where x = 10 wt%, 20 wt% and 30 wt%. The TEC of pristine PBSCF cathode was 23.8 imes $10^{-6}$  K<sup>-1</sup> and for composited with SZM15 addition, namely PBSCF-10SZM, PBSCF-20SZM, and PBSCF-30SZM, respectively were 18.1 imes $10^{-6}$  K  $^{-1}$  , 14.9  $\times$   $10^{-6}$  K  $^{-1}$  , and 12.4  $\times$   $10^{-6}$  K  $^{-1}$  , therefore it was possible to match it with TEC of the chosen electrolyte. In the case of electrochemical properties, similar to results obtained by other authors, in this article, we also can observe that the addition of up to 20 wt% of SZM15 improves the overall performance, whereas 30 wt% gives worse results compared with the pristine cathode. The highest recorded power density equal to 1.64 W·cm<sup>-2</sup> at 700 °C was for NiO-YSZ|YSZ|GDC| PBSCF-20SZM single cell which is around 50 % increase compared to the cell with  $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$  pristine cathode without NTE material addition. Moreover, the single cell with PBSCF-20SZM composite cathode was also examined using 20 %CH3OH-80 %N2 as fuel in a long-term durability test.

Another idea of NTE utilization was proposed by Lu et al., [202] for composite cathodes based on  $Ba_{0.5}Sr_{0.5}FeO_{3-\delta}$  (BSF) - xNdMnO<sub>3- $\delta$ </sub> (NM) for x ranging from 0 to 40 wt%. The optimization of weight percent addition showed that 20 wt% gives the best results. First of all, the TEC was reduced from 27.09  $\times$  10<sup>-6</sup> K<sup>-1</sup> to 16.09  $\times$  10<sup>-6</sup> K<sup>-1</sup>, and the composite cathode layer adhesion improved since the peel strength of the cathode/electrolyte interface increased from 1.73 to 3.23 N·cm<sup>-2</sup> giving around 87 % increase. Also, for this best-optimized composite cathode composition, the authors were able to achieve a peak power density of 1266 mW·cm<sup>-2</sup> at 650 °C giving an 81 % increase when

compared to the pristine cathode. What is more, the authors observed significant improvement in long-term stability tests where thermal cycling was performed. After 23 cycles of rapid heating and cooling, the degradation of the single cell with pristine cathode caused the drop of power density by around 50 %, whereas, for composite cathode with NM negative expansion material addition, it decreased by only 13 %. The authors also presented very uniformly distributed constituents of the composite cathode, which agrees with the stoichiometric composition (Fig. 8f).

Recently Li et al. presented composite cathodes consisting of a typical well-known LSCF material with the SZM15 addition [203]. The authors prepared several cells with different amounts of NTE ranging from 0 to 20 wt%. The TEC of the composites decreased from 18.51  $\times$  10<sup>-6</sup> K<sup>-1</sup> in the pristine cathode to 13.3  $\times$  10<sup>-6</sup> K<sup>-1</sup> for maximum SZM15 addition allowing for matching the TEC with common electrolytes. The electrochemical results have shown that the best results were obtained for 10 wt% addition of SZM15, where PPD reached almost 1200 mW·cm<sup>-2</sup> at 650 °C. What is more, the degradation after 100 h at 600 °C was only around 9 % compared with 34 % registered for pristine cathode without NTE material.

In general, the majority of presented NTE applications were devoted to constructing a composite SOFC cathode, however, there are also some ideas to design and develop a single cell with the same anode and cathode material. The results presented recently by Zhang et al., show the possibility of obtaining the fuel and air electrode consisting of the LSCF, GDC, and NM [204]. For instance, at 800 °C the peak power density for the LSCF@GDC|GDC|YSZ|GDC|LSCF@GDC cell is around  $650 \text{ mW} \cdot \text{cm}^{-2}$ , which is slightly higher when compared to the cell with electrodes with NTE addition, where PPD is 442 mW cm<sup>-2</sup>. Nevertheless, from the applicational point of view, the stability is more crucial than the electrochemical performance (Fig. 8g). In the case of the cell without NTE, at applied voltage of 0.7 V, the current density decreased from 342 mA·cm<sup>-2</sup> to 91 mA·cm<sup>-2</sup>, and in the cell with NM, it decreased from 201 mA·cm<sup>-2</sup> to 196 mA·cm<sup>-2</sup>. Gathered electrochemical performance for solid oxide cells with composite air electrodes with and without different NTEs utilization is shown in Table 2.

Table 2

Comparison of SOCs performance with and without the utilization of NTE materials in composite air electrodes prepared by different authors.

Cell configuration,	Without NTE		With NTE		Ref.
temperature for given PPDs and Rp in symmetrical cell	PPD (mW·cm <sup>-</sup> ²)	Rp (Ω·cm²)	PPD (mW·cm <sup>-</sup> <sup>2</sup> )	Rp (Ω·cm²)	
NiO-YSZ  GDC YSZ  SNC-20SZM, 700 °C	800	~0.036	1220	0.012	[195]
Ni-YSZ YSZ-GDC c- SYNC, 600 °C	~400	0.095	~600	0.075	[192]
NiO–BZCY SDC  BSFCT–20SZM, 650 °C	361	0.797	717	0.277	[193]
NiO-SDC SDC  PBSC–20SZM, 650 °C	1188	0.87	1462	0.117	[194]
Ni-YSZ YSZ GDC  NBC-NM, 700 °C	550	0.725	670	0.712	[198]
NiO-BZCY BZCY BSF- NM, 700 °C	496	0.21	729	0.098	[199]
Ni-BZCY BZCY  BSF–NM, 700 °C	~500	0.21	1170	0.037	[200]
NiO-YSZ YSZ GDC  PBSCF-20SZM, 600 °C	~390	0.41	534	0.15	[201]
NiO-SDC SDC BSF- 20NM, 650 °C	700	N/A	1266	N/A	[202]
NiO-SDC LSCF- 10SZM, 600 °C	572	~1.1	1151	~0.74	[203]

## 7. Conclusion and future perspective

Dozens of years of experiments and investigations focused on negative thermal expansion allowed us to learn how to design, understand, and perfectly utilize materials exhibiting this extraordinary property. First considerations taken more than hundreds of years ago were devoted to explaining negative expansion and how it is affected by external conditions. Later on, scientists described the phenomena of negative expansion and learned how to use it to enhance the properties of already-known solutions or materials. In effect, the improved electrical, magnetic, or electrochemical properties allowed to increase in the quality of devices such as solid oxide fuel cells or solid oxide electrolyzer cells. The problem of commercialization of SOCs, i.e. thermal mismatch between a cathode and an electrolyte is still struggling, however, research articles published in the last few years show that NTE materials can be used as an additive to synthesize composite cathode with adjusted TEC. Therefore, the overall performance of the cell is greater, and what is more, the long-term stability is also visibly increased.

Nevertheless, in the field of NTE materials, there are many experiments to be performed to further enhance the properties of electrochemical, electric, and magnetic devices to improve the quality of already-known solutions in biology, chemistry, and even biomedical fields. However, future research work should focus on tailoring the chemical composition of NTE materials, particularly exploring the chemical modification and doping strategies. Exploring these phenomena will help to adjust the characteristics of thermal expansion with the components of the device, especially the electrolytes, and electrodes for SOCs, where the thermal mismatch persists as a great challenge. Reported works and articles highlight that phase transitions, hybrid frameworks i.e. metal-organic frameworks, and compositional tuning can offer a tractable NTE behavior, which could be significant for future generation and high-temperature devices such as SOCs. The fabrication of multifunctional and advanced NTE materials that exhibit electrical conductivity, magnetism, and superconductivity, can offer amazing possibilities for modern technologies such as smart sensors and spintronics. Furthermore, microstructural and nanostructuring engineering can enable NTE materials to be better integrated with functional phases which will enhance mechanical stability during thermal cycling. Additionally, a deeper insight into the mechanism of atomic level including phonon softening and rigid unit modes is important for leading to the rational design of future-generation NTE materials. Besides the energy applications, the combination of soft and biocompatible materials with NTE ceramics could lead to innovations in drug delivery systems responsive thermal sensors, and biomedical devices. Therefore, for sure, materials with negative thermal expansion will be of great interest in the near future, not only in SOC technology but also in different branches of science, giving many possibilities to increase overall performance.

#### CRediT authorship contribution statement

**Piotr Winiarz:** Writing – review & editing, Writing – original draft, Visualization, Data curation, Conceptualization. **Amir Sultan:** Writing – original draft, Writing – review & editing. **Yihan Ling:** Writing – original draft, Methodology, Conceptualization. **Kun Zheng:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition.

#### Declaration of competing interest

None.

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## Data availability

No data was used for the research described in the article.

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