Proposal Section B. Project Summary.

Thermal expansion is an important materials property from the standpoint of engineering applications, as mismatches in thermal expansion can result in stress, cracks, or separation at interfaces. It is therefore desirable to control and in many cases minimize the thermal expansion of materials. This CAREER proposal is aimed at establishing a basis for the integration of research and education that will lead to the development of materials and composites that can overcome expansion related problems in many applications. Negative thermal expansion (NTE) materials are particularly promising for use in composites, as they are expected to show a more pronounced effect on the composite at equal loading. This proposal seeks to achieve the following specific objectives: (1) To gain a fundamental understanding of factors that influence the expansion and phase transition behavior of NTE materials through the preparation and characterization of new NTE compounds, (2) to characterize the high-pressure behavior of these materials, (3) to prepare NTE/polymer composites with tailored thermal expansion properties, (4) to integrate low temperature approaches used for the synthesis of NTE and other metastable materials into the undergraduate and graduate level chemistry curricula, (5) to realize the participation of undergraduates and high school students in this research, and (6) to enhance the public image of materials chemistry through outreach activities.

The proposed research will *intellectually* contribute to the scientific literature through the preparation and characterization of new NTE materials belonging to the $Sc_2W_3O_{12}$ family. Non-hydrolytic sol-gel routes will be used in the synthesis. This will allow incorporation of cations into the framework that are not accessible by ceramic methods, and straightforward preparation of mixed cation compounds. Analysis by variable temperature powder X-ray diffraction combined with Rietveld refinement will reveal factors that influence the occurrence of temperature-induced phase transitions and the materials' expansion behavior. These results will enable researchers to predict the behavior of both pure and mixed cation systems. The high-pressure stability of the compounds will be established by Raman spectroscopy and synchrotron diffraction studies in a diamond anvil cell. A *second intellectual* contribution will be related to the exploration of NTE/polymer composites in film and fiber form. Special attention will be directed towards the interface region between polymers and oxide particles. The surface of the oxide will be modified by grafting of organic groups that will result in favorable interactions or copolymerization with the polymer precursors. Interface interactions, expansion properties, and changes in mechanical properties of the composites will be characterized.

The *first broader impact* of this proposal will be the integration of advanced materials and low temperature methods used for their preparation into the graduate and undergraduate curricula of the chemistry program at the University of Toledo through the design of a new course in solid-state chemistry. The *second broader impact* lies in the inclusion of powder diffraction methods and analytical tools for powder data ranging from indexing to Rietveld refinement into the existing graduate and undergraduate level Crystallography course. The PI also shares in the responsibility for training researchers on the Department of Chemistry's state-of-the-art powder diffractometer, making her knowledge available to the scientific community at the University of Toledo and local industry. She regularly assists researchers in a variety of standard and non-standard powder diffraction experiments. A *third broader impact* will result from the exposure of undergraduate and high school students to scientific research on projects appropriate for their skill levels. This experience is likely to stimulate their interest in science and will prepare them for choosing a career path. The *final broader impact* will be the enhancement of the public recognition of materials chemistry through outreach activities, using the intriguing concept of materials that shrink when heated, and how their use in composites can help overcome "real-life problems" related to thermal expansion.

Proposal Section D. Project Description.

Description of the career development plan
  Thermal expansion is an important materials property for engineering applications. Mismatches in expansion can result in stress, cracks, or separation at interfaces. Furthermore, precision positioning of components with significantly different expansion coefficients is difficult or impossible for large working temperature ranges. To circumvent these problems, it is desirable to control and in many cases minimize the thermal expansion of materials. This can be achieved through the preparation of composites containing a compound with a low expansion coefficient. Negative thermal expansion (NTE) materials are particularly promising, as they are expected to show a more pronounced effect on the composite at equal loading. Many NTE materials are metastable, requiring low temperature synthetic routes that favor the desired phase. It is the career goal of the principal investigator to develop low temperature approaches for the preparation of advanced NTE materials, to investigate factors that influence their phase stability and expansion behavior, and to incorporate them into controlled thermal expansion composites.

Objectives
  The overall goal of this CAREER development proposal is to further the fundamental understanding of factors influencing the expansion and phase transition behavior of NTE compounds, prepare and thoroughly characterize new NTE materials, and to begin incorporating them into controlled thermal expansion composites. At the same time, the next generation of scientists will be trained in solid-state chemistry and materials' characterization. This will be achieved through the following specific aims:

Specific Aim 1: To elucidate factors that influence the properties of NTE materials. This aim will be achieved through the substitution of a variety of cations into the NTE framework of the $Sc_2W_3O_{12}$ family of compounds, in combination with thorough characterization of the products. A non-hydrolytic sol-gel (NHSG) route will be used for the preparation of the samples. Known ternary compositions, new ternary compositions, mixed cation systems, and materials substituted with aliovalent cations will be investigated. Trends with respect to basic properties of the cations (size, charge, polarizability, electronegativity, etc.), and entropic factors (mixed cation systems) will be determined.

Specific Aim 2: To characterize the high-pressure behavior of NTE materials. The high-pressure behavior of NTE materials is crucial for their use in composites. Characterization will be carried out by Raman spectroscopy and synchrotron powder diffraction. If necessary, high-pressure X-ray spectroscopic methods will be used to follow structural phase transitions and/or amorphization of the compounds.

Specific Aim 3: To prepare NTE/polymer composites with tailored thermal expansion properties. NTE materials have the potential to significantly reduce the thermal expansion of composites without sacrificing the intrinsic properties of other composite components. Polymer films are often used as protective coatings, but suffer from large expansion coefficients, which can lead to "peeling off" of the polymer layer. In order to improve compatibility, NTE particles will be surface modified by silylation. Surface groups will be chosen to allow copolymerization with the desired monomer precursors. Methods for the characterization of the surface modified oxide particles will be developed, and the effect of composite preparation on the properties of polymer films will be established.

Specific Aim 4: To integrate solid-state chemistry and modern low temperature routes to solids into the undergraduate and graduate level chemistry curricula. The existing undergraduate and graduate level chemistry curricula at the University of Toledo will be expanded by a new course in solid-state chemistry. Students will not only learn about classes of solids and traditional preparation methods, but also gain an appreciation of modern low temperature routes and their potential for the synthesis of advanced materials. Examples from the PI's research will be used to illustrate the advantages of low temperature syntheses.

Specific Aim 5: To stimulate the interest of undergraduate and high school students in chemistry. Undergraduate and high school students will be encouraged to conduct research in the field of solid-state

chemistry. In particular, young women will be invited to conduct research in the PI's lab, where they will have interaction with successful female scientists. This experience will contribute to building confidence in their scientific abilities, and should result in enhanced interest and grades in science courses.

Specific Aim 6: To enhance the public image of chemistry and materials science through outreach activities. The potential of NTE materials in composites can be easily explained to non-scientists. NTE presents an intriguing phenomenon that is likely to stimulate the interest of children and adults. Outreach activities will be conducted to excite non-scientists about solid-state/materials chemistry.

Specific Aims 4 through 6 are outlined in more detail in the "**Educational Plan**" section of this proposal.

Significance of the Proposed Research

Thermal expansion is an important intrinsic materials property from an applications point of view. This is especially true for any devices or applications where two different materials are bonded together: Generally, the components will have different expansion coefficients. This can result in thermal stresses at the interface, and ultimately lead to separation and device failure. Significant research has been devoted to the development of low thermal expansion materials for use as length standards (Invar, Fe-Ni alloy, 1897, discovered by Guillaume[1]), in cookware and as mirror substrates (low-expansion glasses and glass-ceramics, developed in the second half of the 20th century[2]). However, modern technology places more severe demands on materials with respect to working temperature range, smaller error margins due to miniturization, and other requirements on materials properties like conductivity, inertness or compatibility with other system components. This makes the development of controlled thermal expansion composites attractive. NTE filler materials have the potential to significantly reduce the overall expansion coefficient of such composites, while minimizing effects on desired characteristic properties of the matrix material.

It is important to understand the factors that influence the behavior of NTE compounds. Not only will this contribute to basic scientific knowledge, it will ultimately allow researchers to predict the properties of compositions that have not been fully characterized. This is especially important for tailoring the exact properties of solid solutions that have mixed cation occupancies, as it is not feasible to prepare and fully characterize every possible cation ratio. If the influence of the individual cations and the effects of cation mixing are understood, an ideal filler material can be chosen for any desired composite.

Composites are an emerging area of scientific research. They offer the possibility of combining advantageous properties from two or more different materials, effectively adding some desirable properties to a composite without interfering with the originally targeted properties of the individual components. Organic-inorganic hybrid materials are a good example of this class of compounds: The organic component is usually chosen for its physical or catalytic properties, while the inorganic counterpart contributes mechanical strength.[3] Controlled thermal expansion composites can benefit many branches in industry through use in protective polymer coatings,[4] molds, mirror substrates, supports for fiber optics gratings,[5] low expansion cement[6] and ceramics,[7] and in the electronic packaging industry.[8, 9]
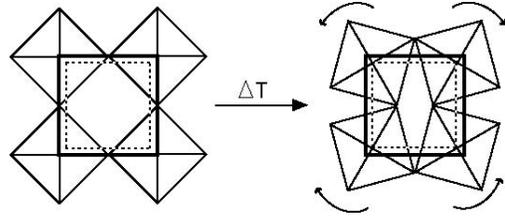
Current state of the field
Negative thermal expansion materials in the $A_2M_3O_{12}$ family

Negative thermal expansion (NTE) materials have received considerable interest during the past decade. There are several oxides that show NTE. The most prominent are the ZrV_2O_7,[10-13] ZrW_2O_8,[14-22] $Sc_2W_3O_{12}$[23-26] and zeolite families.[27-31] The NTE in these materials is an intrinsic property arising from low-energy phonon modes of the low-density crystal structures.[16, 20, 32, 33] Phase transitions can often be correlated to the softening of phonon modes with temperature or pressure. Materials that form with the same structures are expected to show similar expansion behavior. However, the magnitude of expansion, and occurrence of phase transitions, will depend on the identity of the cations that comprise the structure.

In a more visual description, the phonon modes correspond to rigid unit modes (RUMs)[20, 34-36] that cause a concerted tilting motion of the stiff, corner-sharing framework polyhedra (Fig. 1). Like all vibrations, RUMs depend on the mass of the rigid units. Substituting different metals into a structure changes the mass of the polyhedra, and can affect expansion and phase transition behavior. This effect has

been observed in several families of NTE materials. Among them, the $Sc_2W_3O_{12}$ family, represented as $A_2M_3O_{12}$, is most tolerant towards ionic substitution of both the A^{3+} (A = Al, Sc, Y, In, Fe, Cr, small lanthanides) and the M^{6+} (M = Mo, W) sites.[23, 26] A number of materials have been prepared, and it was found that the identity of the A^{3+} cation determines the magnitude of the expansion coefficients along all three crystallographic axes. Furthermore, some compositions show a structural

Fig. 1: Correlated tilting motion of corner-sharing polyhedra can result in NTE.

collapse to a monoclinic phase with a positive expansion coefficient upon cooling. This transition temperature depends on the metals in the structure, and can in some cases be suppressed completely.[26]

There have been some attempts to correlate metal properties with changes in expansion and phase transition behavior. It has been proposed that the expansion coefficients become more negative with increasing size of the A^{3+} cation.[25, 37] Average linear expansion coefficients range from +2.2 ppm for $Al_2W_3O_{12}$ ($r(Al_6^{3+})$ = 54 pm) to –7.0 ppm for $Y_2W_3O_{12}$ ($r(Y_6^{3+})$ = 90 pm). Comparison of the orthorhombic to monoclinic phase transition temperatures of several $A_2Mo_3O_{12}$ compounds also suggests a dependence on the electronegativity of A.[23, 38] However, both of these rules only apply to some $A_2M_3O_{12}$ compositions: $Sc_2W_3O_{12}$ ($r(Sc_6^{3+})$ = 75 pm) has a more negative expansion coefficient than $In_2W_3O_{12}$ ($r(In_6^{3+})$ = 80 pm), suggesting that other factors must also contribute. Similarly, the structural collapse to the monoclinic polymorph is observed at ~550 K for $In_2W_3O_{12}$ (EN = 1.49),[38] and the phase transition temperature can be lowered to 333 K and 408 K by substituting 50% of the In with Sc or Er,[26] which have significantly lower electronegativities (1.20 and 1.11). However, substitution of 50% Al (EN = 1.47) with almost the same electronegativity as In suppresses the phase transition completely above room temperature.[26] $Al_2W_3O_{12}$ itself undergoes the structural change below room temperature. $In_2Mo_3O_{12}$ and $Al_2Mo_3O_{12}$ show more similar transition temperatures of 620 and 480 K.[38] One of our samples, $Y_2Mo_3O_{12}$, adopts the monoclinic structure at room temperature, and transforms to the orthorhombic polymorph at ~300 °C. According to the electronegativity rule, $Y_2Mo_3O_{12}$ (EN = 1.11) should show the lowest phase transition temperature of all molybdates ($Sc_2Mo_3O_{12}$, EN = 1.20, transforms at 180 K[39]). These examples clearly demonstrate that there is a lack of understanding about the factors that influence the properties of $A_2M_3O_{12}$ materials.

High-pressure behavior of NTE compounds

All NTE materials have an open framework structure and low densities.[40-43] The NTE behavior is associated with a softening of phonon modes on compression,[14] which makes them interesting candidates for high-pressure studies. Theoretical predictions for the high-pressure behavior of several compounds are available.[36,44-46] Experimentally, crystalline to crystalline phase transitions and pressure-induced amorphization have recently been observed in several NTE oxides.[17, 22, 47-52] The amorphous phase formed under compression can be viewed as a kinetically trapped intermediate between the starting material and a thermodynamically stable high-pressure phase.[53-55] There has been some discussion about the exact nature of these amorphous phases. Some authors have suggested that amorphization proceeds via uncorrelated tilting motions of the corner-sharing framework polyhedra, leading to loss of long range order.[56] Others have speculated that the process may involve significant changes in cation coordination environment towards those typical in high-pressure phases.[57] Recently, Perottoni *et al.* showed that the amorphous phase formed upon compression of ZrW_2O_8 has a lower entropy than the cubic starting material.[58]

Several materials in the $A_2M_3O_{12}$ family of compounds have been studied by high-pressure Raman spectroscopy. All compounds showed at least one phase transition. High-pressure diffraction data are available for $Sc_2Mo_3O_{12}$,[59, 60] $Sc_2W_3O_{12}$,[49] $Al_2W_3O_{12}$,[52, 61] $Y_2W_3O_{12}$,[62] and $Lu_2W_3O_{12}$.[47] Most of the orthorhombic materials transform to the monoclinic structure that is displayed at low temperatures and ambient pressure by some compositions. At higher pressures, amorphization has been observed for all of these compounds. The phase transitions upon compression can be reversible or irreversible.[62]

Polymer composites

Composite materials based on polymeric matrices and inorganic fillers have tremendous potential for advances in materials performance (e.g., strength, toughness, stiffness, reliability, conductivity).[63, 64]

While polymers have many attractive properties like good processibility, impermeability, chemical resistance and flexibility, they typically exhibit large expansion coefficients. Since mismatches in thermal expansion between two bonded materials can lead to cracks, separation at the interfaces and ultimately device failure, problems arise when coatings are subject to large temperature changes. For example, epoxy resins used as protective coatings in packaging of computer chips exhibit much higher expansion coefficients than silicon. As a result, chips can fail by peeling of the polymer coating as the chip gets hot.

Recently, several approaches have been explored for the preparation of polyimide composites with reduced thermal expansion. These include the incorporation of organoclays or silica particles into polyamic acid blends,[65-68] mixtures of oligomeric silsesquioxanes and polyamic acid blends,[69] AlN nanocomposites,[70] and sol-gel methods to lanthanide complexes in soluble polyimides.[71] High ceramic loadings (30-50 wt%) were necessary to achieve a significant reduction of expansion coefficients, which can affect other polymer properties adversely. Incorporation of NTE materials is expected to show a larger effect at lower loadings, providing a material that retains the required polymer properties (flexibility, ease of coating, impermeability) while displaying reduced expansion. This should reduce overall costs and improve processibility of the composite material. The potential of this approach was demonstrated by Sullivan and Lukehart for ZrW_2O_8/polyimide composites.[4] They found that surface modification of the oxide particles with 3-aminopropyltrimethoxy silane was necessary to avoid phase separation.

Many composites do not show the properties that would be predicted on the basis of the properties of the individual components. The desired effects are often much smaller than expected, and can in some cases be negligible. This is a result of poorly understood and characterized interactions at the interfaces between the different materials. In particular, many polymer composites do not show the expected changes in polymer properties when filler materials are incorporated. A favorable interaction between filler and matrix is necessary to achieve the desired effects. This may require modification of one or more of the starting materials to improve their compatibility. Ideally, a covalent bond between the polymer and the filler particles should be the goal. Such covalent bonds can either be formed by copolymerization, or by post-polymerization reactions similar to crosslinking.

Status of current work

Since my arrival at the University of Toledo in Fall 2003, I have successfully established an active research program in solid-state chemistry. Our lab is well-equipped with a glove box, two vacuum/inert gas manifolds, and a separate oven/furnace room hosting four ovens, four box furnaces and a tube furnace. I am currently supervising two graduate students, two undergraduate students, and one summer high school student. One of my graduate students has begun writing her Master's Thesis, and will graduate by the end of the year. She has been working on particle morphology control and surface modifications of $ZrMo_2O_8$ for use in composites. We will submit at least one publication based on her work within the next six months. We are also in the final stages of analyzing neutron diffraction data on $ZrM_2O_7(OH,X)_2 \cdot 2H_2O$ (M = Mo, W; X = Cl, Br) that we collected at the Intense Pulsed Neutron Source at Argonne National Laboratory earlier this year. These experiments are a follow-up on the results obtained by our high school student during the previous summer, and we anticipate to submit a publication with him as a co-author. We are also analyzing our first set of high-pressure diffraction data, collected on $Ga_2Mo_3O_{12}$ at the Cornell High Energy Synchrotron Source (CHESS) a few weeks ago, and detailed high temperature diffraction data for $Y_2Mo_3O_{12}$. Both projects are anticipated to give publishable results once analysis is finalized. The following paragraphs give a more detailed overview of our research results relating to objectives 1 and 3.

Properties of NTE materials belonging to the $A_2M_3O_{12}$ family

Our group is investigating the use of non-hydrolytic sol-gel (NHSG) methods for the preparation of NTE oxides in the $A_2M_3O_{12}$ family of compounds. Sol-gel methods are powerful techniques for the synthesis of inorganic frameworks at low temperatures, as improved compositional homogeneity of the gel-precursors is obtained compared to traditional ceramic methods.[72] Conventional sol-gel processes start from metal alkoxides, which are dissolved in an anhydrous alcohol. Careful introduction of water into the system initiates hydrolysis and condensation reactions leading to M-O-M bond formation. For ternary oxides, the homogeneity of the gel depends, in many cases, on the relative hydrolysis rates of the metal

alkoxide precursors. If the rates are very different (like for $ZrTiO_4$), the behavior has to be modified by the addition of complexing agents, which slow down the hydrolysis of the more reactive component.

Another possibility is to use a non-hydrolytic sol-gel method. This process depends on condensation reactions between metal halides and ethers or metal alkoxides. The currently accepted mechanism involves a nucleophilic attack of the oxygen donor on the metal atom, followed by cleavage of the carbon-oxygen bond (Fig. 2). This results in different kinetics and reduced dependence

$$(RO)_nM\text{-}\overset{R}{\overset{|}{O}}\text{-}R \quad\quad (RO)_nM\text{-}O\text{-}MX_n$$
$$+$$
$$X_nM\text{-}X \longrightarrow RX$$
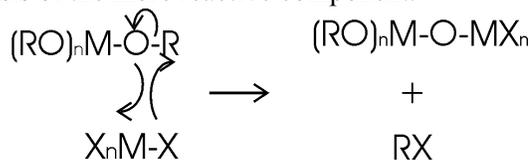
Fig. 2: Mechanism of NHSG reactions.

on the identity of the metal than the cleavage of the metal-oxygen bond occurring in conventional sol-gel processes. NHSG chemistry has been developed as an elegant route to compositionally homogeneous precursors suitable for the preparation of metastable phases.[73, 74] The superior homogeneity of non-hydrolytic gels as compared to conventional gels has been demonstrated for $ZrTiO_4$.[75] Another advantage of this chemistry is that, in many cases, inexpensive transition metal halides may be used as starting materials. The alkoxides can be formed *in situ* by reaction with the ether.

The success of NHSG methods depends on the exclusion of water, which would initiate a conventional sol-gel reaction through hydrolysis and condensation. Metal precursors are stored inside an argon filled glove box, and all manipulations prior to recovery of the raw gels are carried out under air exclusion. Reactions are run in glass ampoules. Metal precursors are dissolved in a non-reactive solvent, and ether is added. After the initial reaction ceases, the ampoule is transferred to a vacuum manifold, cooled in liquid nitrogen, evacuated and sealed. Heat treatment to ~100-170 °C for several days is used to promote the reaction. The resulting amorphous gels or precipitates are recovered in air, and heated to remove residual organics and induce crystallization. Crystalline phases usually form between 300 and 700 °C. In some cases, one of the binary oxides is observed as an impurity phase.

So far, we have mainly focused on the preparation of $A_2Mo_3O_{12}$ compositions with A cations that are known to form the monoclinic or orthorhombic $Al_2W_3O_{12}$ structures (A = Al, In, Sc, Y, Fe, Cr, Yb).[74, 76, 77] While tungstates with all of these A cations have been reported in the literature, data on several molybdates are missing (Y, Yb). Our goal is to better understand variables inherent to the NHSG process, and to optimize the synthetic procedures for a variety of metals. Intrinsic expansion data (determined from variable temperature powder diffraction data through changes in lattice constants as a function of temperature) and phase transition temperatures are not available for all materials. We are collecting data that will close this knowledge gap. As all samples are prepared by NHSG routes and characterized under identical conditions, we will obtain consistent data on expansion and phase transition behavior.

In addition, we have started to extend the selection of A^{3+} cations that can be incorporated into $A_2M_3O_{12}$ frameworks by successfully synthesizing $Ga_2Mo_3O_{12}$. This compound cannot be prepared by ceramic or coprecipitation routes.[26] In our experiment, a suspension of $GaCl_3$ and $MoCl_5$ in acetonitrile was reacted with isopropyl ether in a sealed glass tube at 130 °C for one week. An amorphous powder was recovered, which crystallized to a mixture of monoclinic $Ga_2Mo_3O_{12}$ and MoO_3. This is consistent with elemental analysis, which indicates a slight excess of Mo. High temperature and high-pressure diffraction experiments to investigate the expansion, compressibility and phase transition behavior are currently underway, and we are refining the experimental procedure to obtain $Ga_2Mo_3O_{12}$ without excess MoO_3.

Polymer composites

Controlled thermal expansion inorganic/polymer composites will facilitate the use of polymer coatings in applications where matched expansion coefficients between a material and its protective layer are important. The largest effect of the inorganic filler is expected if covalent bonding is achieved. At identical loadings, NTE materials will reduce the composite expansion coefficient more than a filler with a small positive expansion coefficient. We are collaborating with the Coleman group in Chemical Engineering at the University of Toledo to explore these ideas for $ZrMo_2O_8$/polymer composites.

An important aspect in the preparation of high quality composites is the particle size and shape of the filler particles. Small particles are necessary to get homogenous polymer films and reduce local strain. Since many NTE materials are prone to pressure-induced amorphization,[19, 47, 49, 78] low temperature routes

that produce small particles directly are preferred over traditional ceramic methods followed by ball-milling. Cubic $ZrMo_2O_8$ can be obtained by careful dehydration of $ZrMo_2O_7(OH)_2 2H_2O$.[21] The hydrate precursor is prepared by coprecipitation of water-soluble Zr and Mo species, followed by heating in acidic solution. We have found that the particle morphology depends on the type of acid, acid concentration and heating rate. Agglomerated "beams", facetted cubes and rodlike particles with sizes between 50 by 300 nm and several microns can be recovered. In our hands, the acid counterion influences the particle shape,[79] while nucleation kinetics as a result of the heating rate determine the final particle size. The best approach for highly crystalline cubic $ZrMo_2O_8$ uses perchloric acid, which results in rodshaped particles.

A second crucial factor is the surface compatibility of the polymer and the inorganic filler. Our approach involves surface modification of oxide particles with highly reactive silylating reagents like trichlorovinyl silane. Reactions proceed at room temperature in an inert solvent (e.g., toluene). The organic group on the reagent is chosen to match the monomer precursor, so that copolymerization can be achieved. Preliminary results on composite films suggest that covalent bonding between surface-modified oxide particles and polyvinylester and polyimide polymers has been achieved: No gaps between polymer matrix and filler particles were observed by scanning and transmission electron microscopy for a composite film.
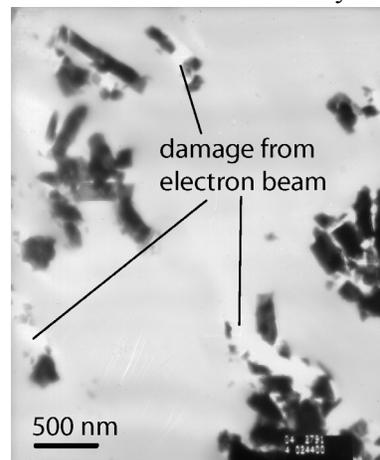
Fig. 3: TEM picture showing good contact between polymer matrix and oxide filler particles.

Objective 1: Elucidation of factors influencing the expansion and phase transition behavior of NTE materials in the $A_2M_3O_{12}$ family of compounds.

As outlined earlier, there is a serious lack of understanding of all the factors that influence the phase transition and expansion behavior of materials in the $A_2M_3O_{12}$ family. We propose to carry out a thorough investigation of factors influencing the behavior of these compounds. This investigation will include both physical properties of the cations and entropic effects in cation mixtures.

Synthesis of ternary compounds. All samples will be prepared by NHSG methods as described above. Since all samples will be prepared and characterized under the same conditions, we will obtain a set of internally consistent data on phase transition and expansion behavior. After finishing the refinement of synthetic variables for the known molybdates we have been working on already, we will prepare the known ternary tungstate compounds. In a second set of syntheses, we will extend the accessible cation selections. There are limitations with regard to the cations that can be incorporated into the framework by ceramic methods, but in some cases they can be overcome by NHSG chemistry, as described above for the case of $Ga_2Mo_3O_{12}$. This set of experiments will include refinement of our initial preparation of $Ga_2Mo_3O_{12}$, its tungsten analogue, and a wider range of rare earth compounds. While review papers state that lanthanides ranging from Ho to Lu can be incorporated into the orthorhombic $A_2M_3O_{12}$ framework, expansion data can only be found for $Lu_2W_3O_{12}$ and some mixed main group/lanthanide compositions.

Based on our initial experiences, the preparation of $Ln_2M_3O_{12}$ may require the use of lanthanide alkoxides or other more reactive compounds instead of halides as starting materials. $LnCl_3$ does not react with diisopropyl ether under NHSG conditions, as evidenced by the presence of lanthanide halides in the powder X-ray patterns of the raw recovered materials. Substitution of alkoxides may also be necessary for some other halides that show poor solubility in "inert" organic solvents (e.g., $CrCl_3$).

Cation mixtures. After establishing appropriate conditions for the ternary systems, we will turn to the preparation of mixed cation systems. In one set of samples, $A_2M_xM'_{3-x}O_{12}$, the M site will be occupied by a mixture of Mo and W. Initially, A will be chosen to represent the "extremes" of accessible cations: Al as the smallest and Y as the largest A^{3+} (or an appropriate lanthanide depending on the outcome of the second set of experiments), Ga as the element with the highest electronegativity, and a lanthanide or Y with low electronegativity. If the investigations on ternary compounds suggest that other factors also correlate with the behavior of $A_2M_3O_{12}$, appropriate elements will be chosen to represent the

6

limits of those parameters. A second and third set of quarternary samples, $A_xA'_{1-x}Mo_3O_{12}$ and $A_xA'_{1-x}W_3O_{12}$, will also be prepared. We will choose mixtures of cations with similar properties for all parameters (Y and Lu, large and low EN; Al and Ga, small and high EN), similar properties for one parameter and dissimilar properties for the other (Y and Sc, different size, both low EN; Al and In, different size, high EN; Sc and In, similar size, different EN), and dissimilar properties for both (Al or Ga and Y). Finally, we will investigate samples with mixed cation occupancies on both the A and M sites. This will maximize entropic effects, which are likely to affect the phase transition and expansion behavior.

Reaction variables. There are several variables that may be fine-tuned to obtain homogenous, high quality $(A,A')_2(M,M')_3O_{12}$ gels. Whenever possible, commercially available metal chlorides will be used as starting materials. In some cases, halides with different oxidation states can show different reactivity, offering a method to control the reaction kinetics (e.g., Cr^{2+} and Cr^{3+}). As the samples are heat treated in air after recovery, oxidation to A^{3+} can occur at this stage. Some lanthanide halides will not react directly with ethers. In these cases, metal alkoxides or other more reactive compounds will be used. Poor solubility of metal halides may also necessitate substitution of alkoxides, as both starting material should show some solubility in the chosen solvent to ensure good homogeneity of the product. NHSG reactions require secondary or tertiary alkyl groups, making isopropoxides or tert-butoxides obvious choices. For many metals, these are commercially available, alternatively, they can be prepared from halides.[80] Diisopropyl ether will be the oxygen source, but other secondary or tertiary ethers can be employed if the reaction outcome is unsatisfactory. The solvent system will be chosen based on the solubility of the metal precursors. Any solvent that will not react with the metal precursors can be used. Common solvents include CH_xCl_{4-x} (x = 0-2), CH_3CN and CS_2. The reaction kinetics will depend on the reaction temperature and the concentration and stoichiometry of the reactants.

Substitution by aliovalent cations. Instead of A^{3+} and M^{6+} cations, the A and M sites in $A_2M_3O_{12}$ can also be substituted by aliovalent cations like in $A_2MP_2O_{12}$ (A = Zr, Hf; M = Mo, W).[26] Recently, substitution of the A site by a mixture of bi- and tetravalent cations was reported by Suzuki *et al.* for $MgHfW_3O_{12}$.[81] It seems likely that a variety of other ions (e.g. Ca, Ti, Pb, Sn, V, Nb, Ta etc.) can be substituted into the flexible $A_2M_3O_{12}$ framework. This will add another entropic factor to the framework structure, as the M site will be occupied by cations with different oxidation states. In addition, we want to attempt the preparation of $AA'M_2M'O_{12}$ compounds, where A and A' are tri- and tetravalent cations, and M and M' are hexa- and pentavalent cations, respectively.

Apart from the $Sc_2W_3O_{12}$ family, there are two other oxide families that show pronounced NTE behavior, the ZrV_2O_7 and the ZrW_2O_8 families. Both $Sc_2W_3O_{12}$ and ZrW_2O_8 contain WO_4 tetrahedra, and the formula contains a tungsten to oxygen ratio of 1:4. As it is possible to incorporate Zr into the $A_2M_3O_{12}$ structure by partial substitution of the M site by P,[82] it would be interesting to investigate the effect of "doping" the A site with Zr without replacing any M site cations. It seems likely that small amounts of Zr could be incorporated, potentially along with A site vacancies, without destroying the structure. Similarly, small amounts of trivalent cations can be substituted for Zr in ZrW_2O_8.[83] It is unclear what will happen for significant amounts of substitution. One possibility would be phase separation into ZrW_2O_8 and $Sc_2W_3O_{12}$ type structures. Alternatively, a "mixed structure" could form at the unit cell level, where features of the ZrW_2O_8 structure (which consists of ZrO_6 units connected to 6 WO_4 units, and WO_4 tetrahedra each connected to 3 ZrO_6 with one dangling oxygen) and $Sc_2W_3O_{12}$ structures (which consists of ScO_6 units connected to 6 WO_4 units, and WO_4 tetrahedra connected to 4 ScO_6) coexist. Another possibility would be the formation of W_2O_7 dimers in the ZrW_2O_8 structure after the introduction of a significant number of oxygen vacancies by substitution of Zr by a trivalent cation. While it is not possible to predict the exact structure that might be formed, there is a good possibility that it will show interesting expansion behavior if it consists of a cornersharing network of WO_4 and AO_6 (A = 3+ and 4+ metals) polyhedra.

Characterization of products. The structure of the products will be characterized by powder X-ray diffraction. We can conduct variable temperature experiments between 80 and 1773 K with instruments available at the University of Toledo. Data will be analyzed by the Rietveld method, providing information about temperature induced phase transitions and the materials' intrinsic expansion behavior. If detailed structural analysis as a function of temperature is needed, neutron data will be

collected at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory to complement the X-ray data. Neutrons are more sensitive to light elements than X-rays, which is advantageous for the analysis of oxygen motions/vibrations as a function of temperature. The Special Environment Powder Diffractometer (SEPD) at IPNS is set up for data collection between 10 K and 1700 K.[84] The lattice constants obtained from the powder data can be used to calculate the intrinsic expansion behavior. Figure 4 shows an example of raw diffraction data, a typical Rietveld fit, and the expansion data extracted.

The crystallization behavior and thermal stability of the products will be analyzed by thermal analysis methods using a combined TG/DTA. Most weight losses will be due to oxidation of residual organics. For many molybdates, TGA also offers a convenient approach to elemental analysis, as MoO_3 becomes volatile at high temperatures. Any excess MoO_3 will evaporate at ~750 ºC, while most $A_2Mo_3O_{12}$ compounds do not lose MoO_3 until temperatures several hundred degrees higher are reached.

Elemental analysis for the tungstate compounds and mixed cation systems will be obtained by Energy Dispersive X-ray Spectroscopy (EDX). Electron microscopy in combination with EDX offers the advantage that the morphology and homogeneity of the materials may be observed simultaneously.

In addition to these "standard" characterization techniques, it is also important to investigate the high-pressure behavior of these open framework compounds, as outlined in objective 2.
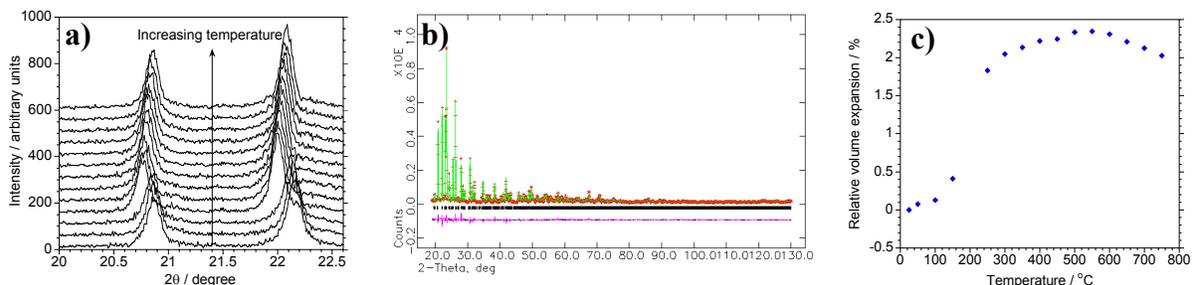
Fig. 4: Expansion behavior of $Al_2Mo_3O_{12}$. **a)** Variable temperature X-ray diffraction data collected between 50 and 650 ºC. The sudden peak shift between the 3rd and 4th scan is indicative of a phase transition. **b)** Full pattern fit obtained by the Rietveld method (structural refinement). **c)** Relative volume expansion plot showing evidence of the monoclinic to orthorhombic phase transition at ~200 ºC. The volume of the orthorhombic cell was doubled for scaling and comparison purposes.

Objective 2: Characterization of the high-pressure behavior of NTE materials.
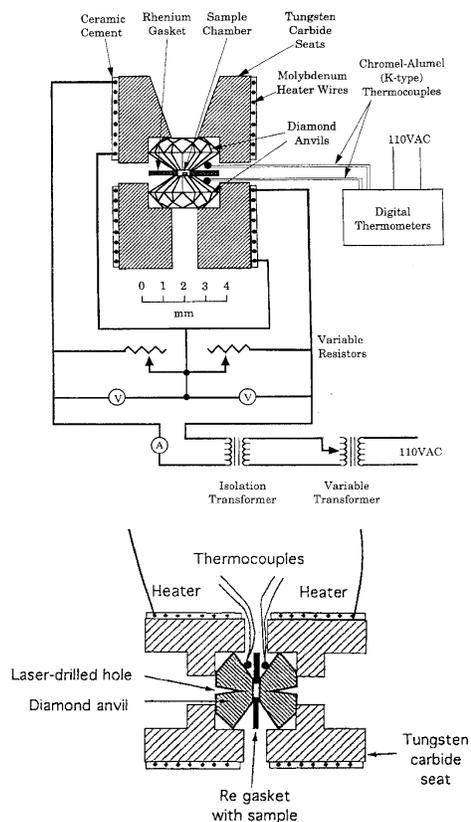
The high-pressure behavior of NTE oxides is not only a scientific curiosity. It is of crucial importance for the preparation and performance of controlled thermal expansion composites, as the NTE material is subjected to pressure during preparation and thermal cycling of composites. Early attempts to prepare Cu-ZrW_2O_8 composites failed because the NTE material cubic ZrW_2O_8 transformed irreversibly to an orthorhombic structure.[9, 85] This clearly demonstrates the need to thoroughly establish the high-pressure behavior of NTE compounds before they can be used in composites. While most materials in the ZrW_2O_8 family of compounds have been subjects of high-pressure studies, structural data at high pressure is available for only a few $A_2M_3O_{12}$ compounds.[47, 49, 60-62] Six different ambient structure types have been reported for $Ln_2M_3O_{12}$ materials alone, suggesting that rich behavior may be found at high pressures.[86, 87]

The best approach to characterizing the high-pressure behavior of our materials is by *in situ* powder diffraction in a diamond anvil cell (DAC). Powder diffraction will show any reversible or irreversible structural changes in response to compression. The experiments can be carried out under hydrostatic conditions by using a pressure transmitting fluid or gas (methanol/ethanol, isopropanol, fluorinert, nitrogen), or under non-hydrostatic conditions by packing the pure oxide powder inside the cell, in which case the pressure is transmitted by grain-to-grain contacts. The hydrostaticity of the pressure medium can result in considerably different behavior.[22] A hydrostatic pressure medium is representative of a composite matrix that is softer than the NTE oxides (e.g., polymers), while ceramic composites are likely to resemble a non-hydrostatic pressure medium. The pressure inside the DAC can be determined by the ruby fluorescence method when small pieces of ruby are included with the sample.
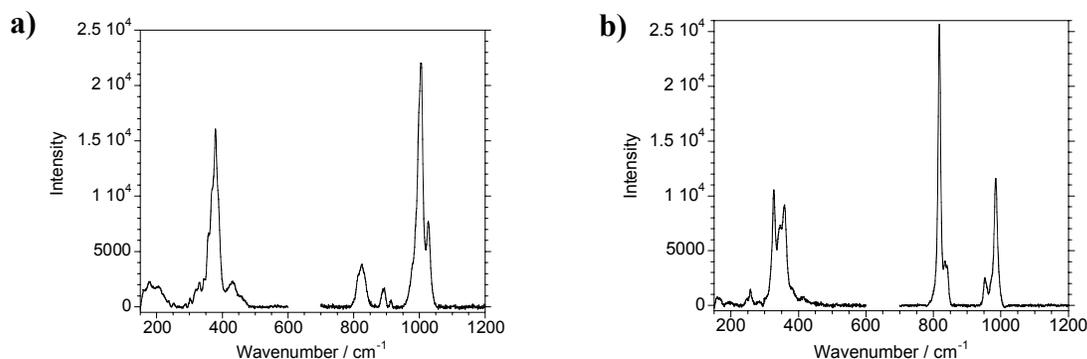
High-pressure diffraction studies require the use of synchrotron radiation to obtain good quality data that allows for full structural analysis. Laboratory diffractometers do not provide enough penetration power with low intensity copper radiation (8 keV). We have previously worked at the B-2 beamline at the Cornell High Energy Synchrotron Source (CHESS), which is optimized for high-pressure experiments. Data are collected either on image plates or more recently with a Mar345 2D detector. A short wavelength (~0.5 Å) is chosen to minimize absorption and compress the data to a smaller angular range, since the downstream cone opening of the DAC is approximately 44 degrees.

As the processing of ceramics-based controlled thermal expansion composites may require high temperatures, it is also important to address the high-pressure behavior of NTE materials at elevated temperatures. We will purchase a custom-designed hydrothermal Bassett-cell (HDAC, Fig. 5), which can reach pressures of 10 GPa and temperatures of 1000 ºC.[88-90] This cell also allows the collection of X-ray absorption spectra at pressure and temperature.[91-93] The diamonds are etched to 80 µm, reducing the distance the X-ray beam has to travel through the diamond by a factor of one half. X-ray absorption spectroscopy (XAS) is carried out at the absorption edges of atoms in the sample and gives information about the local coordination environment of the atom under investigation. The local symmetry and the oxidation state of the atom can be determined from the XANES (X-ray Absorption Near Edge Spectroscopy) portion of the spectra, while information about the nearest neighbor atoms (type, number and distances) can be extracted from the EXAFS (Extended X-ray Absorption Fine Structure) region. Spectroscopic methods offer the advantage of not only being applicable to crystalline materials, but also to samples lacking long-range order, such as glasses or amorphous materials. XAS can provide unique insights into the mechanism[53-55] of pressure-induced amorphization and the crystallization of high-pressure phases upon heating of the amorphous precursor. This technique complements high-pressure diffraction studies, which can only follow structural changes in materials with long-range order. Diffraction methods can only determine the pressure range in which amorphization of NTE materials occurs. XAS can be used to investigate the amorphization mechanism by addressing whether this loss of long-range order involves an increase in the local metal coordination number[57] (in which case the amorphization is likely irreversible), or whether the local environments remain relatively unchanged and amorphization occurs via uncorrelated tilting motions of polyhedra[56] (in which case it may be reversible). Knowledge about the reversibility of pressure-induced changes is important for the application of NTE materials in composites.

Fig. 5: Design of a Bassett hydrothermal diamond anvil cell (HDAC).[90] The diamonds are etched to 80 µm to reduce the absorption of low energy X-rays in the cell.

While high-pressure diffraction studies offer the ultimate structural characterization tool, it is desirable to carry out some preliminary characterization in the lab. Raman spectroscopy in a DAC[94-97] can be used to establish pressure ranges for phase transitions before traveling to a synchrotron, so that these ranges can be carefully targeted during diffraction experiments. This saves valuable beam time and avoids problems with "skipping" an interesting pressure region. Most NTE materials show characteristic Raman modes that change during phase transitions.[16, 98, 99] This allows structural characterization on campus in the laboratory of Dr. Ozan Akkus, who will provide his expertise in data collection and interpretation (see letter of support). Figure 6 shows typical Raman spectra for monoclinic and orthorhombic $A_2M_3O_{12}$ compounds that were collected on his instrument at room temperature and ambient pressure.

Fig. 6: Raman spectra of **a)** monoclinic $Al_2Mo_3O_{12}$ and **b)** orthorhombic $Sc_2Mo_3O_{12}$.

Objective 3: Preparation and characterization of NTE/polymer composites with tailored thermal expansion properties.

Films of controlled thermal expansion polymer composites will be prepared in collaboration with the Coleman group, Department of Chemical Engineering, University of Toledo. We are interested in investigating factors influencing interface interactions, which are of crucial importance for the preparation of high quality composites. In addition, we will work with the Ramsier group in the Department of Physics, University of Akron, on the preparation of NTE/polymer fibers by extrusion methods. The preparation of controlled thermal expansion inorganic/polymer composites is of great economic interest for a number of industries that use polymer supports or coatings. This project is designed to explore possible approaches for the synthesis of such composites, provide an in-depth understanding of important factors influencing the quality of the composites, and establish appropriate characterization techniques.

Compatibility of components: Size and shape. Two factors are expected to have a pronounced influence on composite preparation: The size and shape of the filler materials, and the surface compatibility between the filler and the polymer matrix. It is expected that the mismatch in properties will be significantly reduced by using smaller particles. In addition, small particles are more likely to be homogeneously distributed throughout the polymer matrix, whereas larger particles may show a stronger tendency towards agglomeration and/or settling out. We have successfully managed to prepare rodshaped particles of cubic $ZrMo_2O_8$ with a width of ~50 nm and lengths of a few hundred nanometers. The particles show some tendency toward agglomeration, which we hope to overcome by sonication. Attempts will be made to further reduce the particle size and aspect ratio by increasing the heating rate and changing the acid concentration. Synthesis in organic solvents in the presence of micelle forming species could result in a further reduction of particle sizes.[4] The expansion behavior of $ZrMo_2O_8$ particles with different sizes will be characterized to ensure that the small particles show the expected NTE behavior. We will also investigate the influence of solution additives on the particle shape of cubic $ZrMo_2O_8$. Currently, reflux in perchloric acid offers the best synthetic route, giving material that easily converts to the cubic phase without any amorphous content. Adding salts to the solution can affect the growth behavior of the particles by changing the relative surface energies. Experiments on isostructural $ZrW_2O_7(OH)_2 \cdot 2H_2O$ prepared in HCl and HBr suggest that the halide identity can change the particle morphology. While the small rods are ideally suited for the preparation of polymer fibers by extrusion methods, other particle shapes may be desirable for polymer films.

Surface compatibility. One difficulty with oxides prepared at low temperature results from incompatibility of the OH-terminated surfaces of oxides with many commercial polymers. Modification of the particles is necessary to achieve compatibility of filler and matrix. We have chosen a silylation reaction with highly reactive trichloro-organo-silanes. The reaction proceeds at room temperature in inert solvents and results in the grafting of a significant number of organic groups on the particle surfaces (Fig. 7). Our
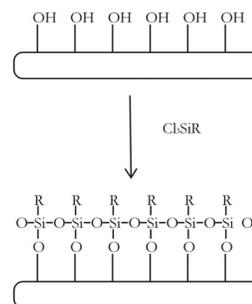
Fig. 7: Schematic of surface silylation.

initial estimates suggest that the surface group density is an order of magnitude higher than reported when using organo-trimethoxy silanes.[4] This should result in stronger interactions between the polymer matrix and the inorganic particles. The organic groups on the silanes are selected to contain a functionality that can be copolymerized with a given monomer precursor. We have chosen vinyl, amine and epoxy groups as our initial targets. These groups achieve compatibility with a large number of industrially important polymers like polyethylene, polyvinyl chloride, polystyrene, polymethyl-methacrylate, polyimides, and epoxy resins. Commercially available trichlorovinyl silane and 4-(trichlorosilyl)-butyronitrile will be used as starting reagents. The vinyl group can be copolymerized directly with monomers containing double bond functionalities, or it can be epoxidized for use in epoxy resins. The butyronitrile group can be converted to an amine group through reduction with $NaBH_4$.

In addition to direct reaction of the surface modified oxide particles and the monomer precursors, it is possible to use oligomers formed by controlled polymerization of the monomers. This is especially advantageous in the polyimide system, where polymerization occurs through the condensation of two different groups (acid anhydride and amine). It is possible to synthesize oligomers with an acid anhydride functionality on both ends. A polymerization reaction of these oligomers with our surface modified oxides can only proceed by covalent bond formation between the oligomers and the oxides, as no other amine groups are available. This is expected to result in excellent mixing between the polymer matrix and the oxide fillers. Different oligomer lengths can be chosen to vary the relative amounts of polymer and filler.

Characterization methods. The as-synthesized $ZrMo_2O_8$ particles will be characterized by X-ray powder diffraction to ensure phase purity. Scanning electron microscopy will be used to observe the particle morphology. The stoichiometry is determined from TGA by evaporation of MoO_3 above 950 °C.

Proper characterization of the surface modified particles poses some challenges. No single method can reliably characterize all aspects that are important in describing the particles. The presence of silicon can qualitatively be detected by EDX in an electron microscope. However, quantification, as well as identification of the functionalities on the organic group, is less straightforward. Some functional groups (triple bond of the nitrile group, double bond of the vinyl group) give weak features in IR spectra, while signals for epoxides and amines are swamped by absorption from the oxide particles. We are planning to establish a protocol for using IR data, CHN analysis, and thermal analysis to gain insights into the identity and number of surface groups. The combination of IR and CHN analysis, together with knowledge about starting materials and reaction conditions, should allow us to unambiguously establish the identity of functional surface groups. Alternatively, surface groups could be removed by laser ablation and detected by mass spectrometry. If the identity of the surface group is known, TGA in air can be used to quantify the number of surface groups, which will be oxidized at temperatures up to 400 °C. Further heating to 1200 °C results in loss of MoO_3, leaving a ZrO_2/SiO_2 mixture in the crucible. Comparison with TGA data from unmodified samples can be used to calculate the $SiO_2:ZrO_2$ ratio, allowing us to cross check our results.

The polymer films will be analyzed by scanning and transmission electron microscopy to determine homogeneity and surface compatibility. Changes in polymer properties (modulus, glass transition temperature, etc.) and expansion behavior as a function of oxide loading will be followed by dynamic mechanical analysis and thermomechanical analysis, respectively.

Educational plan

Materials chemistry is a fast growing field that has developed at the interfaces of Chemistry, Materials Science, and a number of Engineering disciplines. With modern technology requiring more and more advanced materials, the demand for scientists who are well-trained in the preparation and characterization of solids is increasing. Most of these scientists will be recruited from University research laboratories. In particular, the recent incorporation of metastable materials into many technological applications requires scientists who have not only been introduced to traditional solid-state methods (high temperature ceramic synthesis), but are familiar with a variety of so-called "soft chemical" or "chimie douce" approaches (low temperature routes). In addition to synthetic knowledge, characterization of these materials can also pose new challenges. For example, it is well established that a material's properties are intimately related to its crystal structure. Traditionally, structural characterization has been carried out by

single crystal X-ray diffraction. However, many metastable materials, nanomaterials, and composite materials cannot be obtained as single crystals. These materials must be analyzed by powder diffraction. Recent years have seen tremendous progress in the development of both hard- and software for powder based characterization methods. There is a growing demand for scientists who are experts in this field. It is my goal to introduce students to the synthesis and characterization of novel materials both in the class room and in a laboratory setting. Specific aims for my education plan are (i) to maintain a laboratory in which graduate students can receive a broad education in synthesis and characterization of solids by soft chemistry methods, (ii) to offer researchers from a variety of groups a resource for standard and non-standard powder diffraction methods, (iii) to encourage undergraduate and high school students, especially women and minorities, to participate in chemical research to stimulate their interest in science in general and chemistry in particular, (iv) to develop courses in Crystallography and Materials Chemistry, and (v) to improve the public recognition of materials chemistry through outreach activities.

Maintaining an advanced materials laboratory. Research on negative thermal expansion materials, many of which are metastable at room temperature, will expose students to low temperature routes to advanced materials. Coprecipitation routes, hydrothermal synthesis, and techniques for handling air-sensitive materials in glove boxes, Schlenk lines and sealed glassware will be taught. In addition, students will learn to characterize their samples by thermal analysis, electron microscopy and most importantly powder diffraction. Full characterization requires variable temperature X-ray diffraction experiments in combination with Rietveld analysis. If a new polymorph of a material is synthesized, indexing and subsequent structure determination from powder data can be necessary. Specialized experiments like neutron powder diffraction or high-pressure X-ray diffraction will give students exposure to National Laboratories and other synchrotron facilities (the PI has experience at BNL, SSRL, ORNL, ANL and CHESS). This will broaden the students' perspectives, introduce them to sophisticated instrumentation, and establish collaborations with scientists at these facilities that will be beneficial for their future careers. Students will also be able to participate in collaborative research through composite projects or by helping other research groups with non-standard powder diffraction experiments.

Providing an advanced powder diffraction facility. Powder diffraction has undergone significant improvements over the past decade. While most traditional instruments are operated in Bragg-Brentano geometry, users now have a choice of interchangeable Bragg-Brentano, parallel beam, or hybrid optics. The development of fast detectors within the last years has opened up new opportunities for laboratory experiments. The latest generation of laboratory powder X-ray diffractometers offers routine access to variable temperature experiments (including kinetic studies with a fast detector), measurements on air-sensitive or extremely small samples, irregularly shaped samples, thin film analysis, reflectometry, and texture and stress determination all within one instrument. The University of Toledo has recently installed a PANalytical X'Pert Pro system, which can be used for all of the above described experiments. The instrument delivers excellent data quality suitable for structural refinement by the Rietveld method, or structure determination from powder data.

Many researchers are not aware of the information accessible with modern powder instruments. In addition, data analysis beyond simple phase identification requires expertise that I can provide. Theoretical treatment of powder methods, as well as hands-on experiments on indexing and Rietveld refinement, are an integral part of my Crystallography class. The Rietveld portion of the class is open to the University community. In addition, I work with researchers from other groups that are trying to answer non-standard questions by powder diffraction. Examples are the Akkus group in Bioengineering, who are trying to address the relationship between crystallinity/mineralization and fracture toughness of bones, or an investigation of possible decrepitation mechanisms in calcite samples for an industrial client. These collaborative efforts expose my own graduate students to a variety of powder methods, and provide other researchers with an opportunity to explore powder diffraction for their research goals.

Participation of undergraduates and high school students, especially women and minorities, in chemical research. Undergraduate research provides students graduating with a Bachelor's degree with an experience that is beneficial for their transition to traditional industrial jobs, which usually involve a significant amount of laboratory work. It will also facilitate their decision whether they should continue

their studies towards an M.S. or Ph.D. degree. Obtaining a graduate degree in chemistry will in almost all cases require writing a thesis about a research project. In addition, most of the material taught in chemistry classes is ultimately based on theories that were developed from experimental results. It is therefore important to introduce students to the concept of scientific research at an early stage in their careers. Not only can such an experience stimulate their interest in science in general, and chemistry in particular, it will also help them to decide whether a chemistry major or minor is the right choice for them. I am planning to recruit both undergraduate and high school students to work in my lab, either on summer projects or during the academic year. Specific sub-projects will be designed at a level appropriate to the students' scientific background. This will allow students to feel responsible for their own project and build scientific confidence and competence. The field of solid-state chemistry offers unique opportunities for introducing undergraduate or high school students to research, as many projects involve aspects that can be explained on a more general level that does not require an in-depth understanding of complex mathematical or physical theories. At the same time, students are exposed to sophisticated instrumentation for materials' characterization.

Currently, two undergraduate chemistry majors are working in our lab. During the summer of 2004, we hosted a high school junior, Mr. Monty Simon, through Project SEED of the American Chemical Society. Project SEED was created to give students from economically disadvantaged families an opportunity to experience what life in an academic setting is like, and to provide them with mentoring from faculty to help with their future career choices. Many of the students eligible for Project SEED support belong to minority groups. Monty has returned for a second summer under Project SEED, and will enroll at the University of Toledo as a Chemical Engineering major next fall. His work contributed significantly to a poster presented at the European Gordon Research Conference on Solid-State Chemistry, and we expect to publish a paper on the same topic in the near future, on which he will be a co-author. We are planning to submit an application for a Project SEED related first-year scholarship application for Monty. Based on our excellent experiences with Project SEED, we will recruit and host new SEED students in the coming years.

I will also actively participate in recruiting women to conduct chemical research in my laboratory. Being the only female tenure track faculty member in Toledo's chemistry department, this will give students the unique opportunity to work with successful female scientists. Our lab fosters an open atmosphere that welcomes women and minorities, which is obvious from our current group composition: Both of my graduate students are female, one is Caucasian, one African American, one of our undergraduates is female, and both undergraduates and our high school student are African American.

Teaching experience. So far, my teaching experience includes (i) two semesters of graduate level Crystallography, (ii) one semester of undergraduate level General Chemistry, (iii) two semesters of managing a student colloquium series, and (iv) supervision of two graduate, two undergraduate and one high school student in my research laboratory.

Development of graduate level courses. I have taught the department's "Crystallography" course, which covers theory and small molecule methods, in the Fall 2003 and Fall 2004 semesters. This course is offered to graduate as well as undergraduate students. Like all graduate level classes at the University of Toledo, it is offered as a 4-credit hour course. This gave me the opportunity to incorporate many hands-on problems, and several class projects. For example, after introducing symmetry and plane groups, the next lecture was devoted to students marking symmetry elements on wallpapers belonging to the 17 plane groups. I am constantly looking for new hands-on exercises or projects that will improve the class and give students a better idea of how to apply crystallography to real life problems. Last fall, there were three class projects on indexing of powder data, solving a single crystal data set, and refining powder data by the Rietveld method. The Rietveld project was open to the university community.

Last year, the faculty in our department associated with inorganic chemistry discussed the classes that should be offered in the inorganic division. I am planning to develop a course in solid-state chemistry, which could alternatively be taught under our current listing of "Materials Chemistry", a class that has not been taught since I joined the University of Toledo in 2003. This class will cover some traditional solid-state chemistry topics like ceramic methods, basic crystal structures and properties. In addition, a variety

of modern low-temperature, soft chemistry methods, and advanced materials will be introduced. Methods that are important for the characterization of solids will briefly be discussed. This will give students a good overview of "state of the art" materials and methods. Currently, such a class is not offered. The only offering for graduate students with a "Materials Chemistry" major (which is listed as one of the main focus areas of the department) is a Materials Science class, which deals mainly with the engineering aspects of materials like defects, processing etc. The new course will be complementary rather than duplicating this offering.

Improving the public recognition of chemistry and materials science. The field of NTE materials lends itself to outreach activities, as it easily stimulates the curiosity of non-scientists. The potential of materials that shrink when heated can be explained on many different levels depending on the audience, from scientists to elementary school children, as expansion and problems associated with differences in expansion are an everyday-life experience: Freezing water damaging confining containers, problems with telescope or laser setups when the temperature changes the alignment of mirrors, and tooth fillings giving gaps between the filling and the tooth. Negative thermal expansion as a beneficial property can be introduced through water, which causes lakes to freeze from the top and thus allows fishes and other marine life to survive. Based on this, it is easy to see the value of materials that can reduce the expansion coefficient of composites, and thereby control the overall expansion to match that of another material. For secondary school and older audiences, the concept of NTE in open framework structures can

be explained by simple ball-and-stick models containing three atoms as shown in Figure 8. If the sticks are replaced by springs, the differences between positive (soft springs, easy longitudinal motion) and negative thermal expansion materials (stiff springs, difficult longitudinal motion, transverse motion favored) become evident. In my experience, most people show a much more positive attitude towards science when they feel that they understand what the scientists are doing, and how a project or a phenomenon works. This will improve the recognition of materials chemistry as a useful field of study.
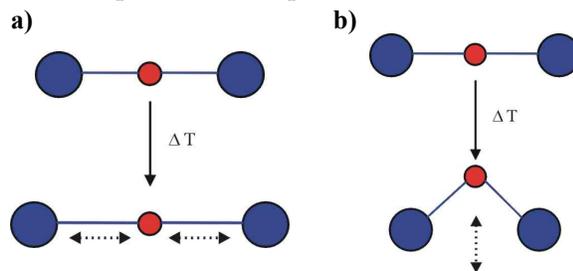
Fig. 8: Expansion explained for three linearly bonded atoms: **a)** Positive (normal) thermal expansion through a longitudinal vibration of the blue oxygen atoms, **b)** negative thermal expansion through a transverse vibrational motion of the blue oxygen atoms.

There are many opportunities to participate in outreach at the University of Toledo. We frequently have high schools visit the department, and the local chapter of the American Chemical Society organizes activities at the Toledo Zoo (National Chemistry Week), in parks, and on campus (chemistry camp for high school seniors). There is also a strong connection to the COSI Museum in downtown Toledo, which organizes and promotes a variety of events throughout the year. I have been in contact with educators at COSI about the possibility of participating in their programs (see letter of support). In December, I will be leading a session on negative thermal expansion materials for COSI's "Dreams to Reality" program, which is designed to attract girls to careers in science and engineering. I am also planning to contribute to the university's Distance Learning program for high school teachers this fall (see letter of support). This will involve the development of a class that combines a large amount of hands-on experimental discovery work with a small lecture/theory component. The topic for my class will be "Expansion". Starting from traditional expansion experiments like thermometer design and calibration, I will be able to not only equip teachers with a hands-on science class, but at the same time give them, and through them their students, a glimpse of cutting edge research by introducing the concept of NTE. I expect that this approach will stimulate the curiosity of the students, and may ultimately help to attract them to scientific careers.

Relation to research goals of the department

The Department of Chemistry at the University of Toledo has two focus areas as identified by the university and the Ohio Board of Regents (OBOR), namely biochemistry and materials chemistry. These two areas are connected through their common interest in crystallography and structural characterization.

In 1996, the OBOR Hayes Investment Fund supported the establishment of the Ohio Crystallography Consortium (OCC) in the College of Arts and Sciences Instrumentation Center through the purchase of two small molecule and one macromolecular diffractometer. Since my arrival at the University of Toledo in Fall 2003, the OCC has expanded significantly through the purchase of a Rigaku FR-E high brilliance microfocused X-ray diffractometer and crystallization robotics system, the installation of a Rigaku R-Axis Rapid diffractometer with a high power Mo rotating anode generator, and the addition of a state-of-the-art PANalytical X'Pert Pro multi-purpose powder diffractometer. I participated in securing the funding for this $247,000 powder diffractometer through the NSF-CRIF program.

The chemistry department is currently expanding, with a target size of about 20 faculty and 75 to 100 graduate students. Several faculty members are actively using crystallographic methods in their research. Drs. Timothy Mueser and Don Ronning are experts in macromolecular crystallography, and our department chair, Dr. Alan Pinkerton, is a distinguished small molecule crystallographer. While the department has always had strong faculty in the field of single crystal structural analysis, it was lacking members with experience in powder methods prior to my arrival in 2003. I have since made my expertise available to a number of research groups within our department as well as in other departments (physics, chemical engineering, biomechanical engineering). The new instrument has seen a tremendous increase in use for both standard and specialized powder experiments. The teaching and research described in this proposal will provide students with the opportunity for training in crystallography and materials chemistry in accordance with the goals of our department.

Dissemination of results

The experimental results obtained in our laboratory will be made available to the scientific community through publication in peer-reviewed journals, presentations at national and international scientific meetings by myself and my students, and seminar presentations in academic departments. We are currently in the process of preparing several manuscripts that will be submitted to journals with international circulation. Some of our results have already been presented at several conferences including the Ohio Inorganic Weekend, a local ACS meeting, and two Gordon Research Conferences. The work conducted in my group will be the basis of my graduate students' theses, which will be available on microfiche after publication.

On the education side, I am constantly improving my class slides, particularly for my graduate level classes, in which I have the freedom to establish the syllabus completely independently. Topics like Crystallography are best taught with PowerPoint slide shows owing to the many complex figures and illustrations. All of my crystallography handouts are available online. In today's society, this makes them available to the broader community. In fact, several faculty and students from other universities have contacted me about my slides. I am planning to follow the same approach for the new Solid-State Chemistry course and any other graduate level courses I will teach.

Previous research and educational accomplishments

My dissertation work at the Georgia Institute of Technology focused on negative thermal expansion materials in the ZrW_2O_8 family, under the supervision of Dr. Angus Wilkinson, a solid-state chemist with special expertise in crystallography, powder diffraction, and synchrotron methods. In particular, we were the first to prepare and characterize cubic $ZrMo_2O_8$. During my postdoctoral fellowship, I was trained in molten metal flux syntheses and the handling of air-sensitive compounds while working on nitrides with Dr. Frank DiSalvo's group at Cornell University. In a second project, we collaborated with the Abruña group on the synthesis of ordered intermetallics for use as direct methanol fuel cell electrodes. In both groups, I was responsible for maintenance and alignment of my supervisors' powder diffractometers and helped other researchers with their powder diffraction experiments.

During my first two years at the University of Toledo, I have mentored graduate, undergraduate and high school students who are conducting research in my laboratory. In addition, I have actively participated in educating users in a variety of standard and specialized methods in powder diffraction.

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