Anisotropic Near Zero Thermal Expansion in $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm, Eu \text{ \& } Yb$) Induced by Structural Reorganization

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Abstract

In this work, we have discovered the anisotropic near Zero Thermal Expansion (NZTE) behavior in a family of compounds $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm, Eu \text{ and } Yb$). The compounds adopt the $CeAl_2Ga_2$ structure type. They were obtained as single crystals in high yield by metal flux growth technique using gallium as active flux. Synthesized compounds with space group $I4/mmm$. Temperature dependent single crystal X-ray diffraction suggests that all the compounds exhibit zero thermal expansion along c direction in the temperature range of 100-450 K. Temperature dependent X-Ray absorption near edge spectroscopic study confirmed NZTE behavior is due to the geometrical features associated within the crystal structure. The anisotropic NZTE behavior was further established by anisotropic magnetic measurements on selected single crystals. The atomic displacement parameters, apparent bond lengths, bond angles, and structural distortion with respect to the temperature reveal that geometric features associated with the structural distortion cause the anisotropic NZTE along c -direction. The preliminary magnetic studies suggest all the compounds are paramagnetic at room temperature except $LaAgGa_3$. Electrical resistivity study reveals that compounds from this series are metallic in nature.

Keywords: Anisotropic Thermal Expansion; Intermetallics; Crystal growth; Crystal Structure; XANES, Magnetism; Resistivity.

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1 Introduction

Thermal expansion (TE) property and differences in thermal expansion coefficients of materials are important in many technological applications ranging from electronic devices to space research. It is a common observation that most of the materials expand upon an increase in temperature, which is known as positive thermal expansion (PTE). The materials with temperature dependent zero thermal expansion (ZTE) or negative thermal expansion (NTE) are scarce and mostly occurs over a relatively narrow temperature window. PTE can be explained well on the basis of population of the higher energy vibrational levels which causes the bond expansion due to asymmetric nature of a typical interatomic potential as are populated.¹ However, many devices that are expected to operate under extreme conditions, for example, low or very high temperature, need to be engineered without any volume expansion and degradation. The materials with NTE or ZTE are highly desirable for both exactitude engineering of various components for nanodevices and of complex bulk systems. The materials demonstrating regular PTE can be tuned with NTE materials to fabricate composites in order to attain an overall ZTE. The ZTE feature hinders materials undergoing thermal shock on hasty cooling or heating. Usually, the NTE feature in materials is crystallographic direction specific. Most of these materials contain elemental silicon and germanium,² Titania–silica glasses,³ carbon fibers, Kevlar and Invar alloys,⁴ ZrW_2O_8 oxides,⁵ certain molecular networks.⁶ The materials $\text{Ag}_3[\text{Co}(\text{CN})_6]$,⁷ Sm_3C_{60} ,⁸ BiNiO_3 ,⁹ MnF_2 ,¹⁰ CuO ,¹⁰ $\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}^{11}$ are also well-known compounds exhibiting NTE.

The materials with anisotropic mechanical, magnetic, optical and elastic properties are well exploited, but the materials with intrinsic anisotropic thermal properties are very rare. Rare

earth based intermetallics are noteworthy in this direction- YbGaGe ,² Yb_4TGe_8 ($\text{T} = \text{Cr}, \text{Ni}, \text{and Ag}$),¹² $\text{Yb}_8\text{Ge}_3\text{Sb}_5$ ¹³ are a few examples reported with anisotropic TE and non-cubic systems with intrinsic anisotropic thermal properties (PTE, ZTE or NTE) need to be discovered. The measure of expansion in a material is given by its coefficient of thermal expansion (CTE). Generally, the compounds having volume CTE in the range of $\alpha_v \approx 10^{-5} \text{ K}^{-1}$ and linear CTE $\alpha_l < |2| \times 10^{-6} \text{ K}^{-1}$ are considered to show very low thermal expansion.^{14,15} There are several aspects which give rise zero and or negative thermal expansion such as structural flexibility in the compounds like LiAlSiO_4 ,^{16,17} α and $\beta\text{-ZrW}_2\text{O}_8$,⁵ magnetovolume effect in the compounds like Fe-Ni and Ni-Cu alloys,¹⁸ $\text{Tm}_2\text{Fe}_{16}\text{Cr}$,¹⁹ $\text{Dy}_2\text{Fe}_{17-x}\text{Mn}_x$ ²⁰ and phase transition in compounds like ZrV_2O_7 .²¹ Herein, we report the $\alpha_v \approx 4.6 - 6.7 \times 10^{-5} \text{ K}^{-1}$ and $\alpha_l \approx -1.3$ to $6.6 \times 10^{-6} \text{ K}^{-1}$ for $\text{REAg}_x\text{Ga}_{4-x}$ ($\text{RE} = \text{Ce}, \text{Nd}, \text{Yb}, \text{and Eu}$) systems in the range of 100 to 500 K which originates due to structural flexibility.

We have chosen the compounds with general formula RETX_3 ($\text{RE} = \text{Rare earth and } \text{T} = \text{transition metals and } \text{X} = \text{Al, Si, Ga, Ge, Sb}$) to study TE behavior. These compounds show interesting physical phenomena due to their adaptation associated with different structure types.²²⁻³⁴ These structural variations in these types are due to the various parameters including valence fluctuations or other electronic transition and or unique geometrical features associated with the structure. These observations motivated us to investigate the temperature dependent thermal properties of these compounds, especially on $\text{REAg}_x\text{Ga}_{4-x}$ compounds. The crystal structure of these compounds was proposed as tetragonal (SG: $I4/mmm$) earlier by Grin et al³⁵ using powder XRD data. However, our single crystal XRD data suggest that they showed unusual thermal parameters in different crystallographic directions. The temperature dependent single crystal XRD on these compounds showed ZTE along c direction and PTE along ab plane

due to the unique geometrical arrangement of atoms in crystal structure in the certain temperature range. A detailed temperature dependent single crystal XRD, anisotropic magnetic studies on single crystals and XANES studies confirm that the geometrical adjustments in the crystal structure along *ab* plane and *c*-direction cause the ZTE.

2 Experimental Section

2.1 Reagents

The *RE* metals (La-Nd, Sm, Eu, Yb, pieces, 99.99%, Alfa Aesar), Ag (shots, 99.99%, Sigma Aldrich) and Ga (pieces, 99.99%, Alfa Aesar) were used as purchased without any further purification. The metals were stored and cut in small pieces inside the glove box.

2.2 Synthesis

2.2.1 Single Crystal Growth

Single Crystals were grown (**Figure S1**) through the metal flux growth technique using gallium as active flux. Plate-shaped single crystals of $REAg_xGa_{4-x}$ were obtained by combining *RE* metal (0.3 g), Ga pieces (2 g), and Ag shots (0.4 g) in a niobium ampoule. The ampoule was inserted in a 13-mm fused silica tube and was flame-sealed under a vacuum of 10^{-5} Torr to avoid any oxidation during heating. The reactants were heated to 1273 K over 10 h to the form melt and then soaked for 2 hrs. Next, the melt was cooled down to 1073 K in 2 h. To get the desired phase formed, the reaction was maintained at this temperature for 48 h. Finally, to grow the crystals, the reaction was allowed to cool gradually to 300 K over 48 h. Since Ga was used as a flux, the product was heated at 673 K and subsequently centrifuged at this temperature through a coarse frit to isolate excess Ga from the product. No reactions between the niobium ampoule and starting materials or product were detected. Residual gallium was removed by immersing the

products in 2–4 M solution of iodine in dimethylformamide (DMF) over 3 h followed by sonication at room temperature followed by drying with acetone. The gray color plate-like crystals of $REAg_xGa_{4-x}$ are 2-4 mm in size obtained in high yield (>90%). Several crystals, which were grown as shining as metallic silver plates, were carefully selected for the elemental analysis, single crystal XRD analysis, anisotropic magnetic measurements. The structure refinement using single crystal XRD resulted in non-stoichiometric composition, which has been taken for the synthesis of the polycrystalline sample in large quantity using the following methods

2.2.2 Arc Melting Technique

The compounds $REAg_xGa_{4-x}$ ($RE = La-Nd$, and Sm) were synthesized using Edmund Buhler GmbH MAM-1 arc melter. The precursors were weighed in the respective stoichiometric ratio (obtained after single crystal refinement) in the Ar atmosphere and repeatedly arc melted (3 times) for maintaining homogeneity. The final products were found to be almost 99.99% yield. The samples were obtained in the form of polycrystalline ingots. After crushing the ingots into a fine powder, samples were used for further characterization.

2.2.3 High-Frequency Induction Heating

The compounds $EuAgGa_3$ and $YbAgGa_3$ were synthesized by high-frequency induction heating. For the synthesis of $EuAgGa_3$, the precursors europium, silver, and gallium were taken in respective atomic ratios (obtained after single crystal refinement) and kept inside a niobium ampoule under an argon atmosphere and subsequently sealed in Edmund Buhler GmbH MAM-1 arc melter. The sealed ampoule was then kept inside a water-cooled sample chamber of Easy Heat induction heating system, Model 7590). The reaction was carried out at 183 Amperes (ca. 1200-1350 K) for 50 min. Finally, the reaction was rapidly cooled to room temperature by

reducing the current to zero Ampere. The light gray colored polycrystalline product EuAgGa_3 was obtained by cutting the niobium tube. No side products and reactions with the ampoule could be detected. Several tests were run for confirming the stability of EuAgGa_3 at two weeks interval for three months and was found to be stable at standard conditions. No more than 1% weight loss was observed in the product. For the synthesis of the YbAgGa_3 compound, the metals ytterbium, silver, and gallium were mixed in tantalum ampoule. The reaction was carried out with the similar procedure for EuAgGa_3 , but applying 170 Ampere current. No side products were detected. The compound YbAgGa_3 was found to be stable for several months. The obtained samples were used for crystal structure determination and physical property studies.

2.2.4 Elemental Analysis

The visibly clean surfaces of single crystals obtained from the flux techniques were analyzed by semi-quantitative microprobe analyses SEM equipped with Bruker 129 eV EDAX instrument with an accelerating voltage of 20 kV in 90 sec accumulation time. The typical image of a plate-like crystal of $\text{REAg}_x\text{Ga}_{4-x}$ ($\text{RE} = \text{La-Nd}, \text{Sm-Gd}, \text{and Yb}$) grown from the flux synthesis is shown in **Figure 1**. The atomic composition of each crystal was found to be close to 1:1:3 by the analysis, which is in good agreement with the single crystal XRD data (**Figure S2**).

2.2.5 Powder XRD

The phase identity and purity of the $\text{REAg}_x\text{Ga}_{4-x}$ ($\text{RE} = \text{La-Nd}, \text{Sm-Gd}, \text{and Yb}$) powder samples were determined using the Bruker D8 Discover diffractometer, set at $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over the angular range of $20^\circ \leq 2\theta \leq 80^\circ$, with a step size of 0.02° at room temperature (297 K) calibrated against corundum standard. The comparison between the experimentally observed and the simulated pattern generated from the single crystal XRD refinement (**Figure S3.1**) confirmed the phase purity. The lattice parameters were determined by

Pawley profile fitting for powder samples of CeAgGa₃ and YbAgGa₃ (**Figure S3.2**) using TOPAS software.³⁶

2.2.6 Single Crystal XRD

Single crystal XRD data of REAg_xGa_{4-x} (*RE* = La-Nd, Sm-Gd, Yb) were first collected at room temperature on selected plate-shaped single crystals using a Bruker Smart-CCD diffractometer equipped with a usual focus, 2.4 kW sealed tube X-ray source with graphite monochromatized Mo-*K* α radiation ($\lambda = 0.7107 \text{ \AA}$) operating at 50 kV and 30 mA, with the ω scan mode. Temperature-dependent data were collected in the range of 100-500 K using a Bruker D8 Venture diffractometer (Photon CMOS detector) equipped with a micro focus, 2.4 kW sealed tube X-ray source with graphite monochromatic Mo-*K* α radiation ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 30 mA, with ω scan mode. Commercially available super glue was used to mount the very tiny plate shaped single crystals on a thin glass (~0.1 mm) fiber. A full sphere having 60 frames was acquired up to 73.28° in 2θ . The individual frames were collected with steps of 0.50° and an exposure time of 10 s per frame. SAINT³⁷ and SADABS³⁸ programs were used to integrate the diffraction profiles and absorption correction respectively. The analyses of systematic absences led us to decide that systems were crystallizing in centrosymmetric tetragonal space group *I4/mmm*. Platon program in WinGx system, ver. 1.80.05³⁹ was employed to check the additional symmetry.

2.2.7 Magnetic Measurements

A Quantum Design MPMS-SQUID magnetometer was used to perform the magnetic measurements. For the measurements, polycrystals obtained from arc melting and induction heating were used after grinding followed by verification of phase identity and purity by powder XRD) Under the applied magnetic field (*H*) of 1 KOe, the temperature dependent data were

collected for Field Cooled mode between 2 and 300 K. Magnetization data were also collected for $REAg_xGa_{4-x}$ at 2 K and 300 K with field sweeping from -70000 Oe to 70000 Oe (**Figure S4**).

The magnetic measurements were also performed anisotropically on single crystals of $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm-Gd, Yb$) grown using metal flux technique. The measurement parameters were the same as were for the polycrystalline samples.

2.2.8 Electrical Resistivity

The conventional AC four probe setup was used to perform the resistivity measurements in the 1T field on $REAg_xGa_{4-x}$ pellets. A strongly conducting silver epoxy paste was adhered to give contacts on the pressed pellets with four very thin copper wires. Commercial QD-PPMS was used to collect the data in the range of 3-300 K. Reproducible results were obtained for several batches.

2.2.9 X-ray absorption near edge spectroscopy (XANES)

XANES experiments at various temperatures on $REAg_xGa_{4-x}$ ($RE = La, Ce, Nd, Eu, \text{ and } Yb$) were performed at PETRA III, P65 beamline of DESY, Germany. Measurements at the Eu L_{III} -edge and Yb L_{III} edge were performed in a transmission mode while measurements at the Ce L_{III} , Nd L_{III} and La L_{III} edge were performed in fluorescence mode at ambient pressure using gas ionization chambers to monitor the incident and transmitted X-ray intensities. A Si [111] double crystal monochromator was used to obtain the monochromatic X-rays which was calibrated by defining the inflection point (first derivative maxima) of Cu foil as 8980.5 eV, ionization chambers filled with suitable gases were used to record the incident (I_0) and transmitted (I_t) photon intensities simultaneously at different edges and a PIPS detector was used for the fluorescent signals. Pellets for the measurements were made by homogeneously mixing the sample with an inert cellulose matrix to have an X-ray absorption edge jump close to one.

3 Results and Discussions

3.1 Structure Refinement

SHELXS 97 was used to solve the crystal structures and SHELXL was used to refine them with anisotropic atomic displacement parameters (ADPs) for all atoms employing full matrix least-squares method.⁴⁰ The crystallographic parameters in the centrosymmetric space group ($I4/mmm$) of the previously reported compound $CeAgGa_3$ ⁴¹ were taken in the insitial step of the refinement to solve and refine the structures of all other compounds $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm-Gd, Yb$). To confirm the precise composition, a discrete series of least square cycles was used to refine the occupancy parameters, The refinement value ($<5\%$) and thermal parameters and bond lengths were found in quite acceptable range. The atomic composition obtained after the structure refinement is non-stoichiometric as the Ag1 and Ga1 atoms are occupied at the $4d$ Wyckoff site. To get a better picture of stoichiometry the Ga2 ($4e$ Wyckoff site) was also mixed with Ag and tried to refine which resulted in unacceptable refinement parameters. At the end of final refinement cycle, we could not get rid of small electron residual densities (less than 9%) in $LaAgGa_3$, $PrAgGa_3$, and $SmAgGa_3$ which is very common to observe as the structure consists of entirely heavy atoms.⁴² The packing diagrams were generated using Diamond⁴³. The data collection, structure refinement, standard atomic positions and ADPs at 293 K of the compounds are listed in **Table 1, S1 and S2**, respectively.

3.2 Crystal Structure

The crystal structure of $REAg_xGa_{4-x}$ along the b direction is drawn in **Figure 2**. The bonds to the RE atoms are not shown to accentuate the three-dimensional $[AgGa_3]$ skeleton. As reported earlier,³⁵ the crystal structures of compounds belonging to $REAg_xGa_{4-x}$ series form a three-dimensional network by comprising of a complex polyanionic network of $[AgGa]^{(2+\delta)-}$

entrenched with *REs*. These networks are pooled through the edges of Ag and Ga atoms along the *ac* plane..

The coordination environments of the constituent atoms in the crystal system are shown in **Figure 3a-c**. The *RE* atoms are surrounded in 8-equatorial capped hexagonal prism environment having coordination number 22 ($\text{Ce}_4\text{M}_8\text{Ga}_{10}$), Ga2 atoms are coordinately surrounded in tricapped trigonal prism manner (M_4GaCe_4) with coordination number 9), while mixed atoms ($\text{M} = \text{Ag} + \text{Ga}$) are in cuboctahedron environment ($\text{M}_4\text{Ga}_4\text{Ce}_4$). Within the first coordination sphere, the average bond distance between *RE* and Ga atoms was calculated to be 3.26 Å. The smallest individual bond distances between *RE* and Ga were found to be 3.3281(14) Å, 3.2876(8) Å, 3.2675(15) Å, 3.2488(3) Å, 3.2168(6) Å, and 3.2382(10) Å for *RE* = La, Ce, Pr, Nd, Sm, and Yb, respectively, near to the calculated ones considering *REs* trivalent atomic radii. The Eu-Ga (3.329 Å) bond distance was found to be larger than the Sm-Ga pair (3.217 Å) that gives an indication towards the oxidation state of Eu ion as divalent which was confirmed by magnetic measurements and XANES study, later. The average bond distance of *RE*-Ga2 and *RE*-Ga1 for all compounds is in the range 3.457-3.260 Å (Ga2 is unmixed, and Ga1 is mixed position). **Table 2** lists the specific bond distances [Å] in the compounds of this series at room temperature with estimated standard deviations.

The unit cell parameters *a*, *c*, *c/a*, $\Delta a/a$, $\Delta c/c$ and volume of the $\text{REAg}_x\text{Ga}_{4-x}$ compounds have been compared in **Figure 4 (a-f)**. The volume of the unit cells was found to be decreasing with the decrease in covalent radii of the *REs*. This can be accounted to the well-known lanthanide contraction. EuAgGa_3 was found to be an exception with an increase in the unit cell volume, which could be due to the divalent nature of Eu. However, interestingly NdAgGa_3 also

deviates from the linearity. Such structural instability was also noticed in the case of NdCuGa_3 and PrCuGa_3 .⁴⁴

Assuming the structural instability based on our previous reports on $\text{REAg}_x\text{Ga}_{4-x}$ compounds,^{35,44} temperature dependent single crystal XRD data at various temperatures (100, 200, 300, 400, 450 and 500 K) have been collected and refined the crystal structure at each temperature (**Table S4 to S11**). Since Ce, Eu, and Yb usually exhibit different oxidation states, unusual temperature-dependent lattice parameters may be attributed to the dependence of their oxidation state. However, it is observed that other compounds also showed similar behavior and may be attributed to the dependence on *RE* atom size, which may be due to the charge transfer between *RE* and Ag or Ga at different temperatures. Close inspection of the data for all the compounds revealed that there is a slight increase in cell volume (**Figure 4c**) and lattice parameter *a* and *b* (**Figure 4a**) with temperature as anticipated by lattice thermal expansion. However, temperature dependent expansion along *c* direction (**Figure 4b**) is negligible which results in a decrease in the *c/a* ratio with an increase in temperature suggesting a strong anisotropy existing in the systems (**Figure 4f**).

The variation in *c* parameter for all compounds within the temperature range 100-450 K has been compared and found almost negligible (**Figure 4b**) suggesting zero thermal expansion² behavior along *c* direction. The driving force for this behavior could be due to one of the reasons

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1. Valence fluctuation as expected in the case of Ce, Eu, and Yb-based compounds²
2. Charge transfer between *RE* and Ag and/or Ga¹²
3. Unique geometric features exhibit in the crystal structure of the compound¹²

To understand the anisotropic thermal expansion behavior due to valence fluctuation or partial charge transfer between *RE* and Ag and or Ga atoms, the magnetic measurements were performed anisotropically along the *c* axis and *ab* plane on the single crystals of CeAgGa₃, PrAgGa₃, NdAgGa₃, and EuAgGa₃. Among all the compounds, CeAgGa₃, EuAgGa₃, and YbAgGa₃ are expected to show variable valences - Ce^{3+/4+}, Eu^{2+/3+}, and Yb^{2+/3+}.⁴⁵ On the other hand, *RE* in remaining compounds expected to exist in the most stable trivalent state. Magnetic measurement is a signature experiment to understand the valence fluctuation with temperature dependent non-linear inverse susceptibility curve. Very interestingly, the inverse susceptibility data of all the samples (**Figure 5**) show a non-linear curve along the *c*-direction and linear trend in *ab* plane, which confirms the anisotropic behavior. The magnetic moment calculated using the formula $2.828 \times \sqrt{\chi_m \times T}$ (where χ_m is a magnetic moment, and T is respective temperature) is tabulated in **Table 5 (Figure 6)** with fitting parameters given in **Table S14**. Relatively large magnetic moment observed along *c* direction for all compounds compared to *ab* plane suggesting the heavy *RE* atoms are orientated along the *c* direction causing hindrance in thermal expansion along *c* direction, which is either due to valence fluctuation or geometrical features associated with the crystal structure. The difference in the magnetic behavior between anisotropic measurements hints towards a slight valence fluctuation playing a role in ZTE along *c* direction. Since there is no abrupt change in the magnetic moments, the probability of ZTE due to valence fluctuation can be ruled out.

To gain more insight on the valence fluctuation, temperature dependent XANES experiment was carried out on *REAg_xGa_{4-x}* involving *RE* = Ce, Nd and La at a temperature of 10 K, 100 K, 200 K and 300 K. These compounds were chosen for this study because Ce is expected to have stable 3+ and 4+ oxidation state, whereas La and Nd has a single stable trivalent oxidation state.

The diamagnetic nature of La and magnetic nature of Nd were utilized for the controlled studies. XANES is a powerful tool to confirm the various elements' valence state in a compound. The amounts of both electronic configurations were estimated relatively by fitting the curves following the previously reported literature.⁴⁶ A peak at 5727 eV in **Figure 7d** corresponds to Ce³⁺ oxidation state. Similarly, a peak at 6215 eV and 5490 eV corresponds to La³⁺ and Nd³⁺ in **Figure 7a and 7g**, respectively. Since there are no profound shifts in the energy of the absorption edge at different temperatures, the ZTE due to valence fluctuation can be ruled out. The temperature dependent XANES measurements support the magnetic measurements as discussed earlier.

In the next step, we have considered the geometrical factors associated within the crystal structures. Since the observed trend is similar in all compounds, NdAgGa₃ has been picked randomly to understand the associated geometrical features. With an enhancement in the M-Ga_{2edge} bond distance from 2.5965(5) to 2.6091(11) (temperature from 100 K to 500 K), surprisingly a negligible increase (~0.0091 Å) was observed for Ga_{2edge}-Ga_{2edge} distance along *c* direction. Similarly there is a linear increase of the bond angles Ga_{2edge}-M-Ga_{2edge} (109.732(14) at 100 K to 110.468(32) at 450 K) and M-Ga_{2edge}-M (70.659(11) at 100 K to 71.025(26) at 450 K) and decrease in bond angles of M-Ga_{2edge}-Ga_{2edge} (125.134(21) at 100 K to 124.766(47) at 450 K) and Ga_{2centre}-M-Ga_{2edge} (109.341(14) at 100 K to 108.975(32) at 450 K) as shown in **Figures 8 and S6**. Similar trends were observed for compounds EuAgGa₃ and YbAgGa₃ as shown in **Figures 8, S7 and S8**. The atomic movement has been meticulously observed (**Figures S6 a-f, S9, Tables 3 and S3**) by being more specific taking the example of NdAgGa₃ in a particular temperature range of 100 – 200 K. Going from 100 K to 200 K, there is an increase of ~0.0091 Å in the Nd_{centre}-Ga_{2edge} bond length, i.e., 3.2415(3) to 3.2506(3) Å. On the other hand,

Nd_{centre}-M distance remains almost the same, i.e., 3.4465(2) to 3.4458(3) Å. The bonds along *ab* plane M-Ga_{2centre/edge} Ag1/Ga1-Ag1/Ga1 and Nd_{corner}-Ga_{2centre} increases respectively 2.5965(5) to 2.5986(4) Å, 3.0029(2) to 3.0128(2) Å and 3.2414(3) to 3.2506(3) Å. Along the *c* direction, Ga_{2edge}-Ga_{2edge} bond distances remain same 2.4408(15) to 2.4406(15) Å, and Nd_{corner}-Ga_{2edge} bond distance decreases by ~0.0126Å (from 4.2089(9) to 4.1963(9) Å). So, the increase in *ab* plane due to Nd_{centre/corner}-Ga_{2edge/centre} is entirely overcome by the decrease in Nd_{corner}-Ga_{2edge} bond if we assume the increase in Nd_{centre}-Ga_{2edge} bond length is due to movement of Ga_{2edge} atom completely in *c* direction (which is obviously not purely) with an enhancement of *c* lattice parameter is 2×0.0126, i.e., ~0.0252Å. Since the *c* parameter is already shortening by ~0.0252 Å so the increase may be occurring in *a* and/or *b* directions. So, it can be concluded that *c* parameter is slightly decreasing going from 100 to 200 K due to compression of Nd_{corner}-Ga_{2edge} bond length and the expansion along *ab* plane is due to increased Nd_{centre/corner}-Ga_{2edge/centre} bond length.

The detailed bond analysis suggests, only the lattice parameters along the *ab* plane are thermally expanding while the atoms in *c* direction are having almost fixed positions resulting in near ZTE. There are two similar atomic arrangements constructing a V-shaped layer along both *a* and *b* directions in zig-zag fashion. For the sake of simplicity, only the top layer has been shown in **Figure 9**. These layers consist of alternate -M-Ga-M-Ga-M-Ga atoms where M = Ag+Ga atoms, while in *c* direction there is a linear arrangement of -RE-Ga-M-Ga-RE- atoms (**Figure 2**). As the temperature increases the atoms lying in zig-zag V-shaped layer start expanding along *ab* plane (shown by dashed arrow in **Figure 9** from the original position; shown by black arrow in **Figure 9**) in such a way that the Ga_{2edge}-M-Ga_{2edge} slab elongates along *ab* plane by adjusting

the angle of Ga_{2edge}-M-Ga_{2edge} while maintaining the thickness of slab Ga_{2edge}-M-Ga_{2edge} almost unaltered. Consequently, the lattice parameter c shows NZTE. -

Based on the above anisotropic near zero thermal expansion observation, the expansivity indicatrix is shown using PASCAL⁴⁷ (**Figure S10**). The coefficient of thermal expansions (CTE) with respect to anisotropic lattice parameter c (α_c) and volume (α_v) are calculated in the temperature range of 100 – 500 K (**Table 4 and S12**). Also, observed and calculated percentage change in the lattice parameters are given in **Table S13**.

4 Physical Properties

The temperature dependent DC magnetic susceptibility measurement was performed on powder samples of all compounds to understand the overall isotropic TE. The anisotropic magnetic behavior was deduced from the measurements on rod-shaped single crystals measured along ab plane and c direction. The measurements were performed at an applied magnetic field of 1000 Oe within a temperature range of 2-300 K (**Figure 10**). The data were fit in the temperature range of 150-300 K in accordance with Curie-Weiss law^{48,49} for all the compounds except YbAgGa₃

The values of observed magnetic ordering and effective magnetic moment μ_{eff} (in Bohr magneton μ_B) obtained by fitting the curves above 150 K are mentioned in **Table 5** for all the compounds which agree to previous report by Grin et al.³⁵ Usually, RE based intermetallics exhibit a slight increase in magnetic susceptibility with increase in magnetic field at lower temperatures, which could be due to magnetic impurities and or crystal field contributions.^{50,51} LaAgGa₃ was found to be diamagnetic in the entire range, and the remaining compounds show weak paramagnetic behavior in the entire temperature range. Except SmAgGa₃ and EuAgGa₃,

the experimental values of μ_{eff} for all compounds agree well with calculated values obtained from Hund's rules for RE^{3+} . For EuAgGa_3 , the magnetic moment (μ_{eff}) $7.9\mu_B/\text{Eu}$ ion confirms the presence of Eu^{2+} valence state and it exhibits antiferromagnetic ordering at 11.4 K. It must be noted that due to the mixing of the excited crystal field levels and lowest lying levels, Sm^{3+} is often show a reduced magnetic moment. And here also, SmAgGa_3 has the room temperature magnetic moment of $1.58\mu_B/\text{Sm}^{3+}$ ion which is in accordance with the fact.⁵²

Also, to get the exact oxidation state of the Eu and Yb in the EuAgGa_3 and YbAgGa_3 , the room temperature XANES data of these two compounds at the RE- L_{III} edge were recorded. The compound EuAgGa_3 exhibit a characteristic signal of Eu^{2+} observed at 6975 eV⁵³⁻⁵⁵ (**Figure 11a**) and a weak shoulder at ~ 6983 eV suggesting the presence of some Eu^{3+} . Area integration under the peaks suggests $\sim 94\%$ presence of Eu^{2+} while $\sim 6\%$ presence of Eu^{3+} corresponding to average Eu valence of 2.06. The ambiguity ($\sim 6\%$) in Eu^{3+} state can be accounted to the several settings used to denote the white-line resonances, edge-step and systematic errors depending upon fitting-model.⁵⁶ This result confirms the predominant divalent nature of Eu, as surmised from the EuAgGa_3 unit cell volume (**Figure 4f**) and the magnetic susceptibility(**Figure 10f**).

Room temperature XANES measurement at ambient pressure was performed for the compound YbAgGa_3 also at the Yb L_{III} -edge (**Figure 11b**). The spectrum shows two absorption peaks centered at 8943.6 (intense) and 8949.6 eV characteristic of Yb^{3+} and Yb^{2+} respectively.⁵⁶ Area integration under the peaks suggests $\sim 77\%$ presence of Yb^{2+} and $\sim 23\%$ of Yb^{3+} confirming YbAgGa_3 as a mixed-valent compound.

Temperature dependent electrical resistivity of the $\text{REAg}_x\text{Ga}_{4-x}$ compounds are shown in **Figure 12** which decrease linearly as the temperature decreases, a typical phenomenon for metallic compounds.^{57,58} The magnetic ordering observed in the magnetic measurements

confirmed with the anomalies in the resistivity data at the corresponding temperature (shown by * in Figure 12). Interestingly, in the case of NdAgGa₃, the anomaly was too weak to observe in the resistivity measurement. The room temperature resistivity of REAg_xGa_{4-x} compounds ranges from 0.88 mΩ.cm (EuAgGa₃) to 6.6 mΩ.cm (CeAgGa₃) is listed in Table 6

Conclusion

In summary, anisotropic near ZTE was observed in the family of REAg_xGa_{4-x} (*RE* = La-Nd, Sm, Eu and Yb) compounds. A combination of various techniques such as temperature dependent single crystal XRD, temperature dependent anisotropic magnetic measurements and temperature dependent XANES confirm that geometric features of the crystal structure play a critical role in the ZTE behavior along *c*-direction. The diverse crystal structures earlier observed in RETX₃ systems from BaAl₄ family were well exploited here to study the ZTE behavior. Since the atom packing in known 15 different crystal structures are very close in nature, it can be concluded that minute symmetry changes responsible for the anisotropic ZTE behavior, which is well explained by temperature dependent single XRD data by considering bond angles, bond lengths, and anisotropic thermal parameters. The present work not only discusses about the anisotropic ZTE behavior but also offers an explicit and inclusive understanding of local structural features of these compounds, which could extend to other members in RETX₃ compounds from BaAl₄ family.

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Supporting information: The Supporting Information is available free of charge on the ACS Publications website at DOI:

X-ray crystallographic file in CIF format; crystallographic tables for crystal data, structure refinement, atomic coordinates and anisotropic displacement parameters; EDX; analyses from powder XRD patterns; magnetization curves; and expansivity indicatrix plot.

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Table 1. Crystal data and structure refinement for $REAg_xGa_{4-x}$ ($RE = La, - Nd, Sm, Eu$ and Yb) at 293 K.

Empirical formula	LaAg _{0.80(2)} Ga _{3.20(2)}	CeAg _{0.83(2)} Ga _{3.17(2)}	PrAg _{0.75(2)} Ga _{3.25(2)}	NdAg _{1.05(1)} Ga _{2.95(1)}	SmAg _{0.97(1)} Ga _{3.03(1)}	EuAg _{0.72(2)} Ga _{3.28(2)}	YbAg _{0.57(2)} Ga _{3.43(2)}
Formula weight	448.50	450.66	448.21	463.18	467.38	458.31	473.86
Wavelength	0.71073 Å						
Crystal system	Tetragonal						
Space group	I4/mmm						
Unit cell dimensions (Å)	<i>a</i> = 4.3637(17) <i>c</i> = 10.768(6)	<i>a</i> = 4.3106(3) <i>c</i> = 10.803(1)	<i>a</i> = 4.2835(5) <i>c</i> = 10.7889(15)	<i>a</i> = 4.2660(6) <i>c</i> = 10.835(2)	<i>a</i> = 4.2133(5) <i>c</i> = 10.847(2)	<i>a</i> = 4.3633(4) <i>c</i> = 10.8576(10)	<i>a</i> = 4.2422(4) <i>c</i> = 10.9824(17)
Volume (Å ³)	205.0(2)	200.74(3)	197.96(5)	197.19(7)	192.56(6)	206.71(4)	197.64(5)
Density (g/cm ³)	7.265	7.456	7.519	7.801	8.061	7.357	7.962
Absorption coefficient (mm ⁻¹)	34.451	35.841	37.310	37.698	40.466	39.179	49.020
<i>F</i> (000)	388	391	390	402	404	397	406
Crystal size (mm ³)	0.10x0.07x0.04	0.10 x 0.07 x 0.09	0.07x0.05x0.08	0.05x0.08x0.07	0.06x0.05x0.09	0.07x0.05x0.08	0.10x0.05x0.08
θ range for data collection	5.041 to 24.864°	3.77 to 30.78°	3.777 to 33.233°	3.761 to 24.918°	3.757 to 24.990°	3.75 to 31.28°	3.711 to 24.957°
Index ranges	-5<= <i>h</i> <=4, -5<= <i>k</i> <=5, -12<= <i>l</i> <=6	-6<= <i>h</i> <=5, -6<= <i>k</i> <=6, -14<= <i>l</i> <=15	-6<= <i>h</i> <=5, -6<= <i>k</i> <=5, -16<= <i>l</i> <=11	-4<= <i>h</i> <=5, -5<= <i>k</i> <=5, -12<= <i>l</i> <=10	-4<= <i>h</i> <=4, -4<= <i>k</i> <=4, -12<= <i>l</i> <=12	-6<= <i>h</i> <=6, -5<= <i>k</i> <=6, -15<= <i>l</i> <=12	-5<= <i>h</i> <=4, -5<= <i>k</i> <=5, -12<= <i>l</i> <=12
Reflections collected	652	1035	915	773	645	1108	664
Independent reflections	70 [<i>R</i> _{int} = 0.1443]	102 [<i>R</i> _{int} = 0.0644]	129 [<i>R</i> _{int} = 0.0944]	71 [<i>R</i> _{int} = 0.0718]	67 [<i>R</i> _{int} = 0.0995]	104 [<i>R</i> _{int} = 0.0721]	71 [<i>R</i> _{int} = 0.0788]
Completeness	92.1%	80.3%	100%	100%	100%	83.1%	100%
Ref. method	Full-matrix least-squares on <i>F</i> ²						
Data / restraints / parameters	70 / 0 / 10	102 / 0 / 10	129 / 0 / 10	71 / 0 / 10	67 / 0 / 10	104 / 0 / 10	71 / 0 / 10
Goodness-of-fit	1.125	1.393	1.188	1.088	1.488	1.187	0.919
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> _{obs} = 0.0483, <i>wR</i> _{obs} = 0.1059	<i>R</i> _{obs} = 0.0345, <i>wR</i> _{obs} = 0.0813	<i>R</i> _{obs} = 0.0525, <i>wR</i> _{obs} = 0.1409	<i>R</i> _{obs} = 0.0206, <i>wR</i> _{obs} = 0.0517	<i>R</i> _{obs} = 0.0666, <i>wR</i> _{obs} = 0.1793	<i>R</i> _{obs} = 0.0214, <i>wR</i> _{obs} = 0.0441	<i>R</i> _{obs} = 0.0299, <i>wR</i> _{obs} = 0.0779
<i>R</i> indices [all data]	<i>R</i> _{all} = 0.0497, <i>wR</i> _{all} = 0.1082	<i>R</i> _{all} = 0.0345, <i>wR</i> _{all} = 0.0813	<i>R</i> _{all} = 0.0527, <i>wR</i> _{all} = 0.1409	<i>R</i> _{all} = 0.0212, <i>wR</i> _{all} = 0.0530	<i>R</i> _{all} = 0.0666, <i>wR</i> _{all} = 0.1793	<i>R</i> _{all} = 0.0214, <i>wR</i> _{all} = 0.0441	<i>R</i> _{all} = 0.0299, <i>wR</i> _{all} = 0.0779
Ext. coefficient	0.015(5)	0.076(11)	0.014(4)	0.016(2)	0.048(2)	0.105(7)	0.020(3)
Largest diff. peak and hole (e·Å ⁻³)	2.825 and -1.457	1.231 and -3.186	6.411 and -3.277	1.613 and -1.612	4.246 and -3.147	2.120 and -1.693	2.311 and -1.556

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| \text{ for } F_o^2 > 2\sigma(F_o^2), wR = \{\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(|F_o|^4)]\}^{1/2} \text{ and calc } w = 1/[\sigma^2(F_o^2) + (0.0359p)^2 + 6.1794p] \text{ where } p = (F_o^2 + 2F_c^2)/3$$

Table 2. Selected bond lengths [$\text{\AA}$] for $REAg_xGa_{4-x}$ ($RE = \text{La-Pr, Sm, Eu and Yb}$) at 293 K with estimated standard deviations in parentheses, where $M1 = Ag1|Ga1$.

Atom Label	d [$\text{\AA}$]	Atom Label	d [$\text{\AA}$]
LaAg_{0.80}Ga_{3.20}		SmAg_{0.97}Ga_{3.03}	
La—Ga2	3.3278(15)	Sm—Ga2	3.2185(6)
La—M1	3.4651(13)	Sm—M1	3.4339(4)
M1—Ga2	2.6173(16)	M1—Ga2	2.5827(8)
M1—M1	3.0856(12)	M1—M1	2.9793(4)
Ga2—Ga2	2.493(5)	Ga2—Ga2	2.436(3)
CeAg_{0.9}Ga_{3.10}		EuAg_{0.72}Ga_{3.28}	
Ce—Ga2	3.2864(9)	Eu—Ga2	3.3252(3)
Ce—M1	3.4545(4)	Eu—M1	3.4812(1)
M1—Ga2	2.6045(12)	M1—Ga2	2.6261(5)
M1—M1	3.0451(4)	M1—M1	3.0816(1)
Ga2—Ga2	2.472(4)	Ga2—Ga2	2.4983(17)
PrAg_{0.75}Ga_{3.25}		YbAg_{0.57}Ga_{3.43}	
Pr—Ga2	3.2665(9)	Yb—Ga2	3.2401(8)
Pr—M1	3.4441(3)	Yb—M1	3.4695(4)
M1—Ga2	2.6001(13)	M1—Ga2	2.6100(11)
M1—M1	3.0289(4)	M1—M1	2.9997(3)
Ga2—Ga2	2.446(4)	Ga2—Ga2	2.450(4)

Table 3. Selected bond lengths ($\text{\AA}$) for $NdAg_{1.05}Ga_{2.95}$ at 100 K and 200 K temperatures with estimated standard deviations.

Atoms	Distance ($\text{\AA}$); 100 K	Distance ($\text{\AA}$); 200 K
Nd—Ga2	3.2415(3)	3.2506(3)
Nd—M1	3.4465(2)	3.4458(3)
M1—Ga2	2.5965(5)	2.5986(4)
M1—M1	3.0029(2)	3.0128(2)
Ga2—Ga2	2.4408(15)	2.4406(15)
Ga2—M1	2.5965(5)	2.5986(4)
Ga2—Nd	3.2414(3)	3.2506(3)

Table 4. The coefficients of linear and volume thermal expansion α_c along crystallographic c direction (CTE) for $REAg_xGa_{4-x}$ ($RE = Ce, Nd, Eu$ and Yb) with their operating temperature range.

Sr. No.	Compound	$\alpha_c (\times 10^{-6} K^{-1})$	$\alpha_v (\times 10^{-5} K^{-1})$	Temperature Range
1	CeAg _{0.90} Ga _{3.10}	-0.42	6.78	100 – 500 (K)
2	NdAg _{0.05} Ga _{2.95}	-1.27	4.67	100 – 500 (K)
3	EuAg _{0.72} Ga _{3.28}	5.71	5.77	100 – 500 (K)
4	YbAg _{0.57} Ga _{3.43}	6.62	5.32	100 – 450 (K)

Table 5. Anisotropic and isotropic magnetic moments of $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm, Eu$ and Yb) with their magnetic ordering temperature. Anisotropic measurements were performed on single crystals grown using the metal flux technique while Isotropic measurements were performed on powder samples.

Sample	Magnetic Moment (μ_B) B.M.				Observed Magnetic Ordering Temp. (K)
	Anisotropic (CW Fit)		Isotropic		
	c	ab	@ Room Temp	CW Fit (150-300K)	
CeAgGa ₃	3.47	2.41	2.7865	2.8	2.69 (T _c)
PrAgGa ₃	4.26	3.91	3.3603	3.3	3.3 (T _c)
NdAgGa ₃	4.3	3.74	3.9218	3.9	43.5 (T _c)
SmAgGa ₃			1.5119	1.5	10.0 (T _c)
EuAgGa ₃	2.94	2.65	1.8436	7.9	11.4 (T _N)
YbAgGa ₃				Temp independent	2.8 (T _c)

Table 6. The resistivity of $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm, Eu, Yb$) at 300K.

S.No.	Material	Resistivity ρ (m Ω -cm)
1.	LaAgGa ₃	1.69
2.	CeAgGa ₃	6.64
3.	PrAgGa ₃	1.13
4.	NdAgGa ₃	2.45
5.	SmAgGa ₃	0.95
6.	EuAgGa ₃	0.88
7.	YbAgGa ₃	0.92

Figures

Figure 1. SEM images of typical $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm, Eu$ and Yb) single crystals grown by metal flux technique.

Figure 2. The crystal structure of $REAg_xGa_{4-x}$ ($RE = La-Nd, Sm, Eu, Yb$) along the b -axis is shown. The unit cell is drawn as solid yellow lines. Zig-zag atomic arrangement of Ag and Ga atoms is seen along ab plane.

Figure 3. The coordination environment of (a) RE ($RE = La-Nd, Sm, Eu, Yb$), (b) Ga and (c) M (Ag+Ga) atoms in $REAg_xGa_{4-x}$.

Figure 4. Temperature-dependent lattice parameters of the compounds $REAgGa_{4-x}$ ($RE = La-Nd, Sm, Eu, Yb$); (a) a and b axes, (b) c axis, (c) c/a , (d) $(a_T - a_{300K})/a_{300K}$, (e) $(c_T - c_{300K})/c_{300K}$ (f) unit cell volume.

Figure 5. Temperature dependence of the inverse anisotropic molar magnetic susceptibility of CeAgGa₃, NdAgGa₃, PrAgGa₃, and EuAgGa₃ at 1000 Oe applied DC magnetic field along (a) *ab* plane and (b) *c* axis. (The insets show anisotropic magnetic susceptibility in the range of 0-15K)

Figure 6. Temperature dependence of the anisotropic magnetic moment (μ_B) of CeAgGa₃, NdAgGa₃, PrAgGa₃, and EuAgGa₃ at 1000 Oe applied DC magnetic field.

Figure 7. Temperature dependent X-ray absorption near edge spectra (XANES); (a-c) LaAgGa_3 at respective edges, (d-f) CeAgGa_3 at respective edges and (g-i) NdAgGa_3 at respective edges.

Figure 8. Temperature-dependent experimental bond distance and bond angle for the compounds $REAg_xGa_{4-x}$ (RE = Ce, Nd, Eu, and Yb). a) The bond distance of M-Ga2_{edge} (M = Ag1+Ga1). b) The bond distance of Ga2_{edge}-Ga2_{edge}. c) The bond angle of M-Ga2_{edge}-M. d) The bond angle of M-Ga2_{edge}-Ga2_{edge}.

Figure 9. Zig-zag atomic layer arrangement along ab plane (the bottom layer has been excluded for the simplicity). The black arrow represents the initial position of the atoms while the dashed arrow represents the movement of atoms along ab plane.

Figure 10. Temperature dependence of the molar magnetic susceptibility of $REAg_xGa_{4-x}$ ($RE = \text{La-Nd, Sm, Eu, Yb}$) compounds at 1000 Oe applied DC magnetic field.

Figure 11. X-Ray absorption near edge spectrum (XANES) for (a) EuAgGa₃ and (b) YbAgGa₃. at Eu L_{III} and Yb L_{III} edges respectively.

Figure 12. Resistivity (ρ) for REAg_xGa_{4-x} ($RE = \text{La-Nd, Sm, Eu, Yb}$) compounds measured as a function of temperature.

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Synopsis

The anisotropic ZTE behavior was observed in a family of compounds $REAg_xGa_{4-x}$ ($RE = La, Nd, Sm, Eu$ and Yb). The geometric features associated with the structural distortion cause the anisotropic ZTE along c -direction.