

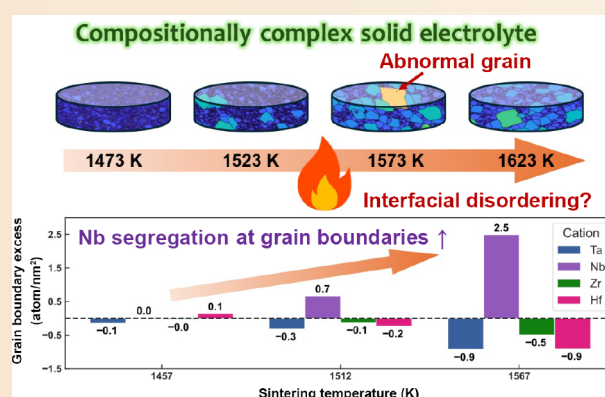
Temperature-dependent microstructural evolution in a compositionally complex solid electrolyte: The role of a grain boundary transition

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Cite this article: Ko S, Du C, Guo H, et al. *J Adv Ceram* 2025, **14**(3): 9221047. <https://doi.org/10.26599/JAC.2025.9221047>

ABSTRACT: Compositionally complex solid electrolyte ($\text{Li}_{0.375}\text{Sr}_{0.4375}(\text{Ta}_{0.375}\text{Nb}_{0.375}\text{Zr}_{0.125}\text{Hf}_{0.125})\text{O}_3$ (LSTNZH) samples are synthesized using different sintering temperatures, durations, and cooling conditions (furnace cooling (FC) vs. air quenching (AQ)). The temperature-dependent grain growth has been examined to investigate the microstructural evolution and the origin of exaggerated (abnormal) grain growth. At moderate temperatures, the grain growth of LSTNZH follows a cubic root growth model with an Arrhenius temperature dependence. With increasing temperature, bimodal microstructures develop, and the Arrhenius temperature dependence breaks down. Notably, increasing the temperature induces increased Nb segregation at general grain boundaries (GBs), in contrast to classical GB segregation models but suggesting premelting-like GB disordering, which can explain the observed abnormal grain growth (AGG). In addition, the large grains become faceted with increasing temperature, which occurs concurrently with the temperature-induced transitions in GB segregation and grain growth, thereby further supporting the occurrence of a GB phase-like (complexion) transition. The impacts on the densification, ionic conductivity, and hardness are also examined. This work provides a new insight into the fundamental understanding of the grain growth mechanisms of the emergent class of medium- and high-entropy compositionally complex ceramics (CCCs), which is essential for tailoring microstructures and material properties.

KEYWORDS: compositionally complex ceramics (CCCs); solid electrolytes; perovskite; grain growth; grain boundary (GB); electron backscatter diffraction (EBSD)



1 Introduction

Li-ion solid-state electrolytes with fast Li^+ transport can replace flammable organic liquid electrolytes in commercial Li-ion batteries to enable safer solid-state batteries (SSBs) [1,2]. In recent decades, inorganic oxide-based solid electrolytes (OSEs) have drawn much attention in the development of SSBs because of their high ion transference number (i.e., the ratio of the current from Li-ion transport to the total electric current), excellent thermal stability, and chemical stability. Here, the three classes of well-studied material systems are garnet-type [3], NASICON-type

[4,5], and perovskite-type [6] OSEs. During the synthesis and processing of polycrystalline OSEs, grain boundaries (GBs) and pores are introduced, which are often more resistive, thereby deteriorating the overall ionic conductivity [7]. Generally, microstructures can significantly influence the overall ionic conductivity and mechanical properties. A desirable solid electrolyte should display a room-temperature ionic conductivity higher than 10^{-4} S/cm, good mechanical integrity against scratches (high hardness) [8], and high toughness to prevent Li dendrite penetration under high current densities [9]. Although a pressure-assisted sintering process, such as spark plasma sintering and hot

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Received: September 24, 2024; Revised: February 10, 2025; Accepted: February 11, 2025

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pressing, has been well adopted to create dense sintered pellets [10–14], microstructural engineering through doping to simultaneously promote densification and grain growth in pressureless sintering is a more cost-effective and practically preferred method to reduce total GB resistance and improve the critical current density [15,16]. For example, prior studies reported that doping garnet solid electrolytes with Ba²⁺, Ta⁵⁺, and/or Nb⁵⁺ increased the sintering density and grain size [16–18].

In addition to conventional doping strategies, high-entropy ceramics (HECs) represent an emergent class of ceramic solid solutions with high ideal configurational entropy of mixing [19,20], which introduces new opportunities and vast compositional spaces for material discovery. Most prior studies of HECs investigated equimolar five-component HECs, including perovskite [21], rock salt [22], fluorite [23], pyrochlore [24] oxides, borides [25–28], and silicides [29–31]; see Refs. [19,20] and references therein.

In 2020, Wright *et al.* [19,32] further proposed broadening HECs to compositionally complex ceramics (CCCs), where nonequimolar compositions, as well as long- and short-range ordering, which reduce configurational entropies, can provide additional opportunities to tune and improve properties.

In 2023, Ko *et al.* [33] discovered a series of nonequimolar compositionally complex perovskite oxides (CCPOs) as Li-ion solid electrolytes. They revealed that the improvement in GB ionic conductivity was driven by increasing grain size. Specifically, the reported total ionic conductivity of a medium-entropy CCPO (Li_{0.375}Sr_{0.4375})(Ta_{0.375}Nb_{0.375}Zr_{0.125}Hf_{0.125})O₃ (denoted as LSTNZH) reached ~0.15 mS/cm at room temperature, with an average grain size > 3 times larger than that of its baseline compound (Li_{0.375}Sr_{0.4375})(Ta_{0.75}Zr_{0.25})O₃ (denoted as LSTZ; with a total ionic conductivity of 0.094 mS/cm at room temperature) synthesized under the same conditions [33], differing from the sluggish grain growth reported in other HECs [34–38]. A recent study further investigated the microstructural evolution and ionic conductivity of CCPOs in two-dimensional (2D) compositional space [39]. The enhanced grain growth in LSTNZH was found to be caused by Nb addition [33,39]. However, the underlying mechanism remains elusive, which motivated this study.

In this study, we discovered that grain size enlargement in the CCPO LSTNZH is driven by abnormal grain growth (AGG). It is not uncommon to observe AGG in perovskite oxides (e.g., SrTiO₃ (STO) [40], BaTiO₃ (BTO) [41], (K,Na)NbO₃ [42], and Li_{3-x}La_{2/3-x}TiO₃ [43]). Here, Li_{3-x}La_{2/3-x}TiO₃ (LLTO) is a perovskite-type solid electrolyte that possesses high GB resistance that limits the total ionic conductivity [6]. The total ionic conductivity of LLTO can be increased to 10⁻⁴ S/cm through AGG, triggered by transient planar defects or single-crystal templating [44–46]. Hence, the effective volume fraction of resistive GBs is reduced, thereby increasing the total ionic conductivity. In general, the origins of AGG are attributed to (i) the broad or bimodal distribution of initial powder particle/grain sizes (with some particles/grains larger than twice the critical radius) [47–49], (ii) the presence of impurities and secondary phases [50–54], (iii) anisotropic GB mobility or GB energy [55], (iv) texture [56], and (v) GB complexion (phase-like) transitions [57–61]. Specifically, it has been shown that the transitions of grain growth kinetics can be related to GB transitions involving the presence of two types of GBs with different mobilities in perovskite [43,62] and other [57–61] oxides, resulting in bimodal microstructures. AGG is typically considered detrimental because it can often result in increased coarsening and reduced densification during sintering, leading to increased porosity, decreased hardness, and decreased ionic conductivity [63,64]. However, Zeng *et al.* [65] employed

AGG to produce dense garnet solid electrolytes with coarse grains for improved air stability and ionic conductivity. Furthermore, AGG was used to promote exaggerated grain growth in perovskite-type LLTO to reduce GB resistance [44–46]. Although AGG is present in various perovskite oxides, the corresponding root causes can differ. Moreover, AGG in the emergent class of HECs and CCCs and their underlying mechanisms have not yet been studied, calling for a fundamental investigation.

In this study, we utilized electron backscatter diffraction (EBSD) to characterize the microstructures of a medium-entropy CCPO, (Li_{0.375}Sr_{0.4375})(Ta_{0.375}Nb_{0.375}Zr_{0.125}Hf_{0.125})O₃, or LSTNZH, to study temperature-dependent grain growth. Microstructural evolution and AGG are linked to nanoscale GB structures, as investigated via aberration-corrected (AC) scanning transmission electron microscopy (STEM) in conjunction with energy dispersive spectroscopy (EDS). We found an unusual temperature dependence of GB segregation, i.e., more pronounced Nb segregation at higher temperatures, in contrast to the classical GB segregation models. This suggests the occurrence of premelting-like GB disordering at high temperatures. Consequently, the enhanced kinetics at disordered GBs can cause AGG. This work provides new insights into the fundamental understanding of microstructural evolution, particularly the mechanisms of AGG, in CCCs and HECs. The microstructural effects on ionic conductivity and hardness, two useful functional properties for inorganic solid electrolytes, are also evaluated.

2 Materials and methods

2.1 Material synthesis

The samples were synthesized via planetary ball milling and pressureless sintering, similar to what has been reported in the synthesis of LSTZ-based perovskite oxides [66,67]. The precursors, Li₂CO₃ (99.999%; Acros Organics, USA), SrCO₃ (99.99%; Alfa Aesar, USA), Ta₂O₅ (99.993%; Fisher Scientific, USA), Nb₂O₅ (99.9%; Alfa Aesar, USA), ZrO₂ (99.9%; US Research Nanomaterials, USA), and HfO₂ (99.99%; US Research Nanomaterials, USA), were mixed with isopropyl alcohol as a process control agent (PCA) at a 1:1 ratio of powder to solvent by weight. The slurry mixture was ball milled via a low-energy planetary ball mill (PQ-N04, Across International, USA) at 300 r/min for 24 h (45 min of milling with a 15 min resting interval, repeated 24 times), with yttria-stabilized zirconia (YSZ) used as the milling media and jars. The PCA was dried overnight in the oven. The particle size distribution of the as-milled powders was quantified via a dynamic light scatterometer (Litesizer 500, Anton Paar, Austria), which revealed a size range of 636–953 nm (Fig. S1 in the Electronic Supplementary Material (ESM)). The powders were ground again with a mortar and pestle and calcined at 800 °C to convert carbonates into the oxide form. The green pellets were subsequently formed by pressing the calcined powders in a 10 mm diameter die via a regular hydraulic press at 130 MPa for 2 min. The sintering process was performed in a high-temperature box furnace at nominal temperatures ranging from 1200 to 1350 °C isothermally for various durations between 4 and 24 h, with a ramp rate of 5 °C/min. For air quenching (AQ), the samples were quickly removed from the furnace, with an approximate overall cooling rate of 40 °C/min from the sintering temperature to room temperature (while the initial cooling rate was higher). The as-sintered pellets were polished before characterization.

We designed three series of experiments, including samples sintered at different temperatures with furnace cooling (FC) and air quenching (AQ) (denoted as the “temperature-FC series” and

the “temperature-AQ series”, respectively) and samples sintered for different durations with FC (denoted as the “time-FC series”).

2.2 Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on 30 mg of the as-milled powder mixture via a thermal analyzer (SDT 650, TA Instruments, USA). The heating profile was ramped from room temperature to 1400 °C with a ramp rate of 5 °C/min in compressed air to mimic the possible reactions and phase transformation occurring during calcination and sintering.

2.3 Ionic conductivity and hardness measurements

The sintered pellets were coated with Ag paste on both sides as ion-blocking electrodes. The impedance spectra of the pellet samples were measured with an impedance analyzer (4194A, Hewlett-Packard, USA) from 100 Hz to 40 MHz, with an applied voltage amplitude of 100 mV at room temperature. On the basis of a prior study [33], the applied bias voltage of 100 mV is small enough for LSTNZH to ensure linearity and better comparison for different samples.

Vickers microhardness tests were conducted on a Leco microhardness tester with an applied load of 1 kgf (≈ 9.8 N) on the samples mounted in epoxy. The average Vickers hardness of each sample was calculated from the diagonal of thirty individual indents under an optical microscope. Nanoindentation was performed via a nanoindenter (G200, Agilent, USA) equipped with a diamond Berkovich tip. A 10×10 array of indentations was created for each sample, except that a 10×5 array was used for 1623K-12 h-FC. The distance between the two nearest indents was 20 μm . A maximum load of 98 mN was used with a peak hold time of 10 s.

2.4 X-ray diffraction

Ex situ X-ray diffraction (XRD) patterns of the precursors, calcined powders, and sintered pellets were collected with an X-ray diffractometer (MiniFlex, Rigaku, Japan; Cu K α radiation $\lambda = 1.5406$ Å; scan rate = 2.3 (°)/min; step = 0.01°). For the *in situ* XRD experiment, a green pellet was formed using the same procedure for pressureless sintering. *In situ* XRD was performed with an X-ray diffractometer (SmartLab, Rigaku, Japan) with a 2.2 kW Cu K α X-ray generator (40 kV, 44 mA) and Bragg-Brentano optics equipped with a high-temperature furnace (Rigaku, Japan) at 1400 °C (mounted on a θ - θ goniometer). The green pellet was placed on an alumina stub inside a platinum holder and heated from 800 to 1350 °C in the air at 50 °C intervals between isothermal temperatures. The temperatures were stabilized for 10 min before each XRD scan. A heating/cooling ramp rate of 5 °C/min was used throughout the experiment. The 2θ scan range for XRD was 20°–80° (3.0 (°)/min), with a step size of 0.02°.

2.5 Microstructure characterization

The polished surface imaging, porosity, and elemental distribution at the micron scale were characterized by scanning electron microscopy (SEM; Apreo LoVac, Thermo Fisher Scientific, USA) with EDS on a detector (X-Max 80, Oxford Instruments, UK) operated at 6.4 nA and 20 kV. The relative density was converted from the porosity, which was quantified by ImageJ on the basis of the brightness and darkness contrast of the SEM images in forward scatter detector (FSD) mode. The elemental quantification was based on Sr-La, Nb-La, Zr-La, Ta-La, Hf-La, and O-K α . EBSD was conducted via an SEM (Apreo LoVac,

Thermo Fisher Scientific, USA) equipped with an EBSD detector (Symmetry, Oxford Instruments, UK) operated at 51 nA and 20 kV. To ensure sufficient statistics for measuring the grain size, we followed the ISO 13067:2020 standard for each sample in the furnace cooling series [68]. To determine the appropriate step size for bimodal grain size distribution quantification in the air quenching series, we adopted a convergence test on the change in mean grain size upon step size selection (Fig. S2 in the ESM). The final step size used was determined by the converged step size value for each air-quenched sample, where the mean grain size became independent of the step size. Around 1500–3000 grains were quantified with a step size equal to or smaller than 100 nm, as suggested by Rheinheimer *et al.* [69]. The area-weighted grain size distributions, shape factors, misorientations, and GB plane distributions (GBPDs) were analyzed via the MATLAB-based MTEX toolbox [70].

2.6 Transmission electron microscopy (TEM)

TEM samples were prepared through mechanical polishing via an allied multiprep polishing system (MultiPrep™ System-8", Allied High Tech Products, USA) with subsequent ion milling under argon (Ar) via a precision ion polishing system (model 695, Gatan, USA). TEM lamella of the 1512K-12 h-AQ sample (sintered at 1512 K for 12 h, air quenched) were prepared via the focused ion beam (FIB) method on a dual beam system (Quanta 3D FEG, Thermo Fisher Scientific, USA). High-angle annular dark-field (HAADF) STEM imaging and STEM-EDS measurements were carried out on a high-resolution transmission electron microscope (HRTEM; JEM-ARM300F Grand ARM, JEOL, Japan) operated at 300 kV and equipped with double aberration correctors and dual 100 mm² Si drift detectors (SDDs). The procedures for calculating the atomic percentages and GB excesses of B-site cations at the GBs via STEM-EDS are described in Method (I) in the ESM.

3 Results and discussion

3.1 Phase formation and isothermal grain growth

In this work, we aimed to elucidate the origin of AGG in LSTNZH. LSTNZH green pellets were created from the calcined powder mixtures, which had an intermediate phase matching the crystal structure of LiNbO₃ with R3c, as shown in Fig. S3 in the ESM. Subsequently, the LSTZ-type cubic perovskite phase (*Pm* $\bar{3}$ *m*) formed via solid-state reactions upon high-temperature (reactive) sintering. Since phase formation is involved in the initial stage of sintering, understanding the onset temperatures of solid-state reactions is essential for determining the appropriate sintering temperature range (after the cubic perovskite phase forms). Hence, we carried out TGA and DSC on the as-milled precursor powder mixtures (Li₂CO₃, SrCO₃, Ta₂O₅, Nb₂O₅, ZrO₂, and HfO₂) heated from room temperature (RT) to 1400 °C (Fig. 1(a)). The major weight losses occur in the ranges of (i) RT–568 °C and (ii) 568–850 °C. In the low-temperature range (i), the 4.73% weight loss can be attributed to the removal of moisture and PCA used during ball milling. In the intermediate temperature range (ii), a subsequent weight loss of 6.73% and an endothermic peak on the DSC curve are observed. According to the reported calcination reactions, the Li₂CO₃ precursor decomposes into Li₂O and CO₂ between 600 and 700 °C, whereas the strontium carbonate precursor decomposes into SrO and CO₂ at 900–1100 °C [71,72]. The endothermic peak at 568–850 °C indicates heat adsorption due to carbonate decomposition reactions. Nevertheless, the reactions are not fully complete (as the

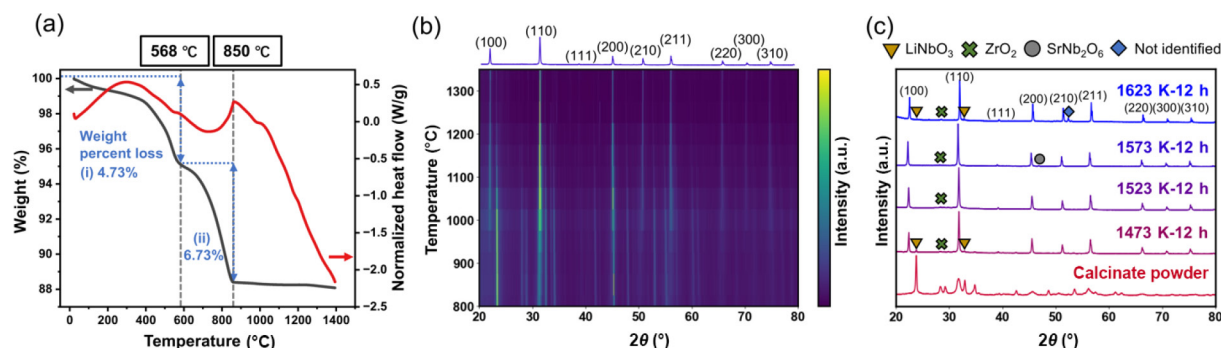


Fig. 1 (a) TGA and DSC of as-milled powder mixture from room temperature to 1400 °C to mimic the solid-state reactions occurring during conventional sintering. (b) *In situ* XRD patterns of green pellet from 800 to 1350 °C. (c) *Ex situ* XRD patterns of four furnace-cooled samples sintered for 12 h at 1200 °C (1473 K), 1250 °C (1523 K), 1300 °C (1573 K), and 1350 °C (1623 K).

theoretical weight loss due to the release of CO₂ is 10.87 wt%). Moreover, the reaction from the precursors to the intermediate phase also occurs in stage (ii). Above 850 °C, the exothermic peak with only a slight weight change implies a phase transformation, forming the cubic perovskite phase. During synthesis, the as-milled powder mixture was calcined at 800 °C for 2 h, where the carbonates were partially transformed into oxide forms and participated in the solid-state reaction, so the as-calcinated powder mixture pattern did not match the phases of the precursors or the phase of the cubic perovskite (Fig. S3 in the ESM). The phase evolution upon ramping from 800 to 1350 °C was investigated from the *in situ* XRD patterns in Fig. 1(b). The peak intensity of the (110) plane at $2\theta = 31.4^\circ$ becomes stronger above 1100 °C with a narrower peak width, which indicates the crystallization of the cubic perovskite structure. The intermediate phase peak at $2\theta = 23.4^\circ$ is suppressed above 1200 °C. Accordingly, the phase stability temperature window is confirmed to be between 1200 and 1350 °C, where the XRD peaks match the *ex situ* XRD pattern of LSTNZH at 1300 °C (*Pm*3*m*). The secondary phases (HfO₂, ZrO₂, LiTaO₃, and LiNbO₃) are found in *ex situ* XRD patterns of the LSTNZH samples sintered from 1200 to 1350 °C for 6 and 12 h, and 1200 °C for 4–24 h (Fig. 1(c) and Fig. S4 in the ESM). Owing to Li evaporation, the formation of trace secondary phases is inevitable for Li-containing compounds under high-temperature processing. According to the Rietveld refinement results shown in Figs. S5 and S6 in the ESM, the secondary phases for the sample sintered at 1473 K for 24 h were identified as 18.6 wt% LiNbO₃ and 0.5 wt% ZrO₂.

We selected 1473 K (1200 °C) as the sintering temperature for isothermal grain growth kinetics investigations (for the time-FC series) because it is the lower limit of the phase stability temperature window to prevent severe Li evaporation during prolonged sintering. EBSD was used to quantify the grain size statistics, with the standard setup shown in Fig. 2(a). Figures 2(b)–2(e) show the microstructural evolution at isothermal sintering durations of 4, 8, 14, and 24 h at 1473 K in the time-FC series. The grain size statistics quantified by EBSD are documented in Table S1 in the ESM. An abrupt increase in the grain size is observed in the sample sintered for 24 h (Fig. 2(e) and Fig. S7 in the ESM), where the mean grain size changes to $4.13 \pm 3.65 \mu\text{m}$ (vs. $2.32 \pm 1.9 \mu\text{m}$ for the 20 h sample). Although anomalous large grains (> 9 times larger than the mean value) are also observed in the 20 h sample (Fig. S8 in the ESM), their influence on the overall grain size distribution is insignificant due to their low fraction. The large grain population becomes pronounced in the 24 h sample and leads to a broad grain size distribution (Fig. S9(d) in the ESM), where a bimodal microstructure with two grain

populations is developed. Figure S10 in the ESM shows the change in the mean grain size as a function of sintering time. A sudden jump in the mean grain size from 20 to 24 h suggests the occurrence of nucleation-limited interface-controlled growth [73]. Once the driving force for grain growth exceeds the critical energy required to nucleate on a new growing facet, the abnormal grains grow rapidly and turn into faceted rectangular-like shapes. To quantify the shape change, we used circularity as the shape factor [74], which is defined as the ratio between the actual grain perimeter and the equivalent perimeter. Figures S9(e)–S9(h) in the ESM display a shift in circularity from a perfect circle ($f_{\text{circ}} = 1$) in the samples with larger grain sizes due to the change in curvatures and faceting, which serves as a driving force for AGG [75].

To quantify the grain growth rate, we analyzed the relationship between the grain size and time to calculate the kinetic constant of grain growth. Since the initial sintering process involves phase formation and grain growth, we take four hours as the reference (start) time (t_0), at which time the solid-state reaction has been completed. Hence, the material is mostly homogeneous at $t = t_0$. The grain growth rate of normal grains can be described as Eq. (1):

$$d^n - d_0^n = k(t - t_0) \quad (1)$$

where n represents the grain growth exponent, d represents the mean grain size at the nominal sintering time (t), k represents a grain growth constant, and $(t - t_0)$ represents the time interval for grain size to increase from d_0 at t_0 (~1 μm at 4 h) to d at a sintering time of t . To consider only the grain growth kinetics of normal grains in the LSTNZH, the 24 h sample (with AGG) is excluded from the fitting dataset. We compared the fitting results when $n = 2$ and $n = 3$. The latter results in a better R -square value of 0.95. Accordingly, $(d^3 - d_0^3)$ is expressed as a linear function of $(t - t_0)$ with a fitted k of $2.1 \times 10^{-22} \text{ m}^3/\text{s}$ at 1473 K (Fig. 2(f)). This value is one order of magnitude lower than that of high-entropy oxide (Mg,Co,Ni,Zn)Ti₂O₅ ($2.18 \times 10^{-21} \text{ m}^3/\text{s}$ at 1473 K) [38]. The mean grain size increases with the cubic root dependence (grain growth exponent $n = 3$) of time, as shown in Fig. S10 in the ESM. The slow (normal) grain growth kinetics can result from the drag effect from pores, solute drag, and/or Zener pinning [47,51,76].

The effect of the grain size on the total GB ionic conductivity is illustrated in Fig. 2(g). Through impedance measurements of the Ag-coated pellets under an AC current, the bulk ionic conductivity was probed in the high-frequency range, whereas the GB component was present in the intermediate-frequency range. The bulk and GB resistances were fitted via the equivalent circuit

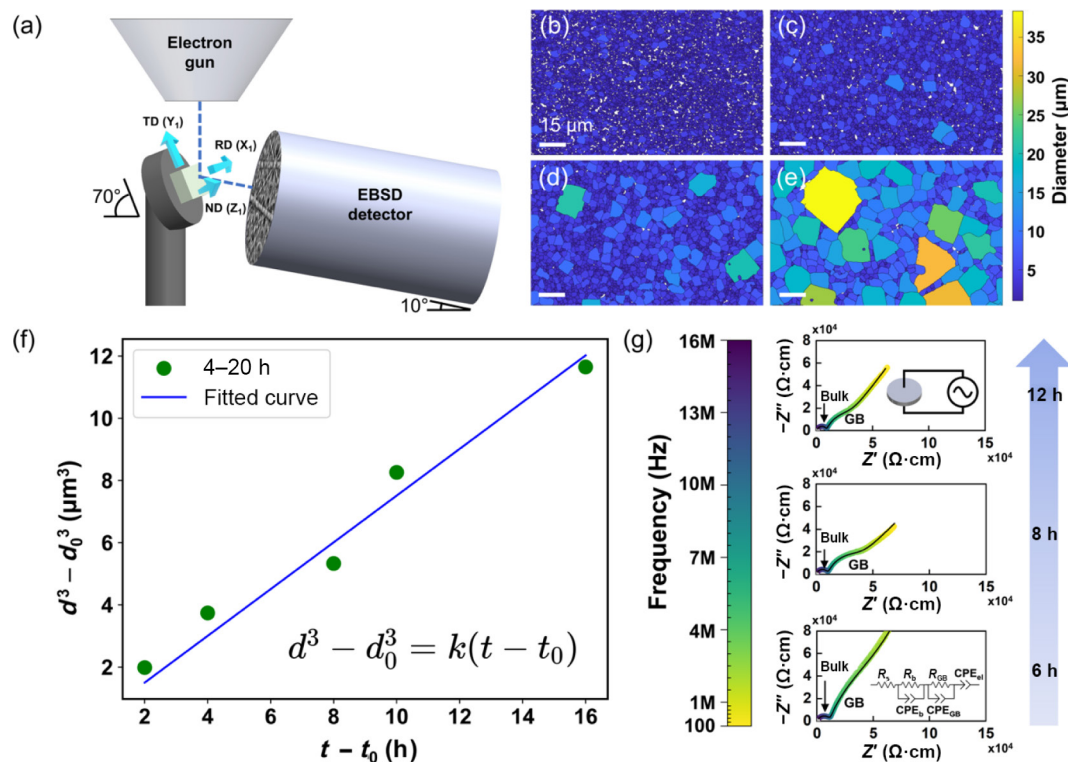


Fig. 2 (a) EBSD experimental setup. EBSD grain maps color-coded according to grain diameters of samples sintered at 1473 K for (b) 4 h, (c) 8 h, (d) 14 h, and (e) 24 h, respectively. (f) Fitted linear relationship of $(d^3 - d_0^3)$ vs. $(t - t_0)$. (g) Impedance spectra of LSTNZH sintered at 1473 K for 6, 8, and 12 h, with the fitting curves. Insets in panel (g) show impedance measurement setup and equivalent circuit model.

Table 1 Summary of room-temperature bulk, GB, and total ionic conductivities of furnace-cooled LSTNZH samples sintered at different temperatures and durations in this work

Sintering condition	1473 K			1523 K		1573 K		1623 K	
	6 h	8 h	12 h	6 h	12 h	6 h	12 h	6 h	12 h
Bulk ionic conductivity (mS/cm)	0.092	0.112	0.126	0.225	0.187	0.211	0.357	—	—
Apparent GB ionic conductivity (mS/cm)	0.018	0.054	0.074	0.049	0.096	0.140	0.335	—	—
Specific GB ionic conductivity (mS/cm)	8.419×10^{-5}	4.016×10^{-4}	3.394×10^{-4}	3.266×10^{-8}	1.746×10^{-4}	1.012×10^{-3}	7.669×10^{-4}	—	—
Total ionic conductivity (mS/cm)	0.015	0.037	0.047	0.041	0.063	0.084	0.173	0.129	0.033

Note: —: The bulk and GB ionic conductivities cannot be deconvoluted.

model with two RC circuits in series via a brick layer model [77,78], where the fitted impedance and nonideal capacitance values are shown in Table S2 in the ESM. The calculated bulk, apparent GB, specific GB, and total ionic conductivities are summarized in Table 1. The decrease in the GB resistance with increasing sintering time from 6 to 12 h can be attributed to the reduction in the total volume of resistive GBs.

3.2 Temperature effect on grain growth and microstructural evolution

We examined the effect of temperature on the grain growth kinetics of LSTNZH in the temperature-FC series, and the grain size statistics are documented in Table S3 in the ESM. Figure 3(a) shows the EBSD inverse pole figures (IPFs) of LSTNZH sintered from 1473 to 1623 K for 6 and 12 h, respectively. According to the grain size distribution histogram (Fig. S11 in the ESM), the grain size distribution is nearly unimodal at 1473 K for 12 h. The sample sintered at 1523 K for 12 h has a bimodal distribution of grain size and a duplex microstructure composed of large abnormal grains in a fine-grained matrix (Fig. 3(a)). The profile becomes skewed to the large-grain-size end at 1573 K for 12 h.

We adopted the cubic-root-of-time relationship shown in Fig. 2 to plot the increase in the mean grain size as a function of $1000/T$ (Fig. 3(b)), following a temperature-activated Arrhenius-type expression (Eq. (2)):

$$\ln(d^3 - d_0^3) = \ln(k_0 t) - \frac{Q}{RT} \quad (2)$$

where d is the mean grain size at 12 h, d_0 is the reference mean grain size at 6 h, k_0 is the proportional constant, t is the time for grain growth (6 h in this case), Q is the activation energy of the temperature-activated process, R is the gas constant, and T is the absolute temperature. The dashed line represents the linear dependence of $\ln(d^3 - d_0^3)$ and $1000/T$ below 1523 K. Notably, samples at 1573 K were excluded from the fitting because the presence of an increasing fraction of abnormal grains caused uncertainty in determining the isothermal grain growth rate via the cube rule. Although abnormal grains are also present in the 1523 K samples, their influence on the average grain size is insignificant due to their small fraction. The air quenching series at 1457 and 1512 K are included in Fig. 3(b) and have the same temperature dependence as the furnace cooling series.

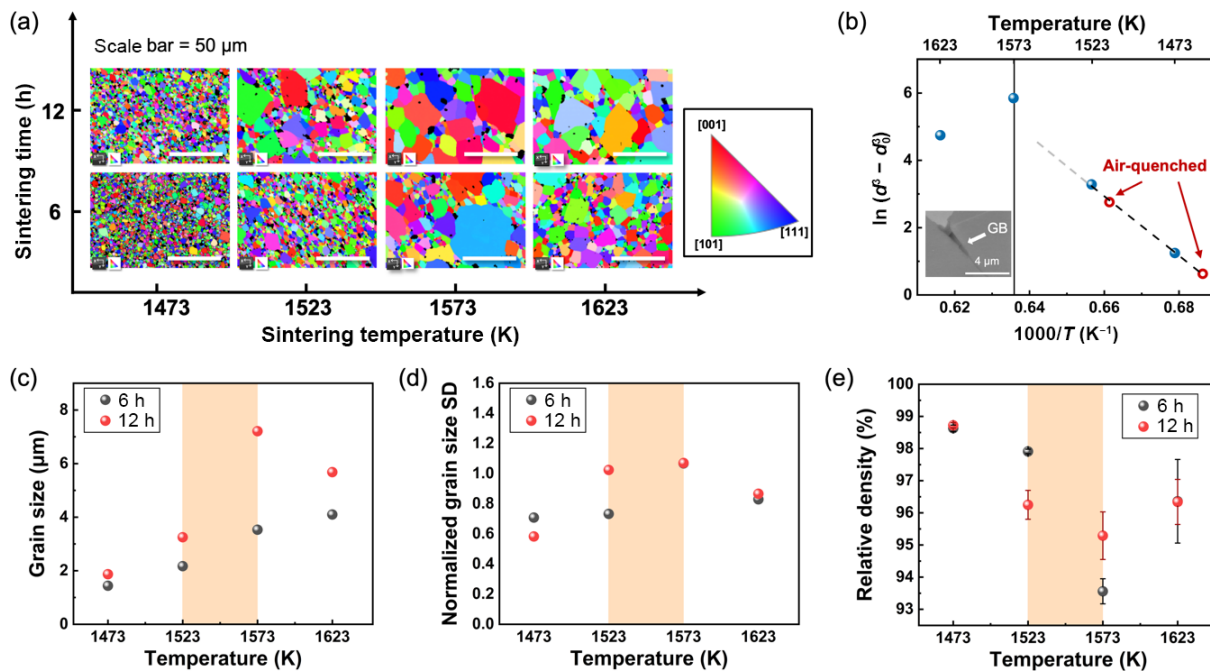


Fig. 3 (a) EBSD IPFs (normal direction) of LSTNZH sintered at 1473, 1523, 1573, and 1623 K for 6 and 12 h, respectively, with an IPF color key. (b) Temperature-induced grain growth behavior (red open circles: air-quenched series). (c) Mean grain size (d_{avg}) and (d) normalized grain size standard deviation (SD) of temperature-FC series at 6 h (gray dots) and 12 h (red dots). (e) Corresponding relative density with measurement error bars of ± 1 SD. Dashed lines in (b) represent fitting lines of Arrhenius-type activation process.

Accordingly, the activation energy is fitted from the four samples at 1457–1523 K, showing a value of 7.61 ± 0.2 eV ($R^2 = 0.99$), which is comparable to that of STO (7.5 eV) [69]. The light gray dashed line represents the fitting line extrapolated to 1573 K, which displays a noticeable increase in the microstructural evolution rate of the 1573 K samples from the temperature dependence below 1523 K.

The grain growth rate further decreases at 1623 K together with the Nb-rich precipitates found along the GBs, as shown by the dark contrast in the backscattered electron images in the inset of Fig. 3(b) and Fig. S12 in the ESM. SEM-EDS elemental maps (Figs. S13 and S14 in the ESM) reveal Sr deficiency and Nb and O enrichment in the region of the GB precipitate phase. We compared the atomic percentage change throughout the five selected sites (locations) in Fig. S15 and Table S4 in the ESM. At Sites 1 and 3, where the dark Z-contrast was found, the Nb signals accounted for 12.8 at% and 11.9 at%, respectively. On average, Nb is 2.5 at% higher than Ta at the precipitate sites. A decrease in the ratio of Sr/B cations and Sr/O is observed (Table S5 in the ESM). In contrast, Sites 2, 4, and 5 represent the stoichiometric LSTNZH primary phase, with Nb approximately 1 at% lower than the Ta for each site. Hf and Zr are equimolar throughout sites 1 to 5 (only 0.2 at% difference), regardless of the Ta and Nb atomic percentages. Figures S16 and S17 in the ESM also indicate that the formation of the Nb-rich GB precipitate becomes pronounced with increasing sintering temperature and time. We further used EBSD to confirm that the precipitate phase at a triple-grain junction was LiNbO_3 (Fig. S18 in the ESM), with a low melting point of 1523 K. Therefore, the liquid phase might exist at and above 1573 K. GB wetting in liquid phase sintering can lead to AGG in $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$ [79–81]. However, the liquid phase does not contribute to a faster growth rate or larger average grain size in LSTNZH. This can be attributed to the increasing fraction of solid secondary phases due to the deviation in stoichiometry, which can pin the motion of GBs.

We note that transitions in the grain growth kinetics with increasing temperature, similar to those shown in Fig. 3(b), are commonly observed in perovskite oxides, such as STO, BTO, and LLTO. Within the temperature range between 1623 and 1698 K in STO, a decrease in the grain growth rate is associated with the transition of the dominant GB type from fast complexion to slow complexion at elevated temperatures, leading to bimodal microstructures [43,69]. In addition, Ti-rich wetting films were found at GBs in LLTO above the transition temperature of 1673 K [43].

To show the presence of abnormal growth, Fig. S19 in the ESM presents the change in their normalized grain size distribution over time. During normal grain growth, the normalized grain size distribution should achieve a self-similar “normal” profile (a narrow distribution with a single maximum) independent of time. In contrast, the broadening of the normalized distribution or occurrence of a bimodal distribution can be categorized as AGG [82]. Following these criteria, the grain size distributions at 1473 and 1623 K are normal, whereas those at 1523 and 1573 K are abnormal. Notably, the profile of the 1573K-12 h sample changes back to a normal distribution. This is because the exaggerated growth slows down when abnormal grains impinge, similar to the abnormal/normal transition reported in austenitic stainless steel [47,83]. Therefore, the two populations merge back to one as the sintering time increases to 1573 K.

The quantified grain size statistics as a function of the temperature of the eight temperature-FC series samples are shown in Figs. 3(c) and 3(d). A linear dependence of the mean grain size on temperature is observed in the 6 h samples, whereas increased grain growth occurs in 1573 K-12 h samples, leading to an increase in the mean grain size by ~ 2 times that of the 1573 K-6 h samples. The corresponding normalized grain size standard deviation is defined as the ratio of d_{sd} to d_{avg} . The results show large differences between the 6 and 12 h samples at 1523 and 1573 K. This change is correlated with the bimodal and skewed

distribution of grain sizes in this temperature range, suggesting AGG.

The reduction in relative density from 1473 to 1573 K is another indication of AGG. The diffusion of atoms across GBs changes the grain size, whereas the diffusion of atoms along GBs results in densification [84]. When AGG occurs between 1523 and 1573 K, the GBs of abnormal grains have higher mobility and can pass through pores readily. The closed pores are left behind in abnormal grains, thereby leading to a decrease in relative density. The increase in density from 6 to 12 h at 1573 K can be attributed to pore elimination in the final sintering stage. The forward scatter diffraction images shown in Fig. S20 in the ESM illustrate the removal of GB pores from 6 h to 12 h.

At 1623 K, the normalized grain size distribution returns to a normal profile.

3.3 Temperature-induced abnormal grain growth and bimodal microstructures

We quenched LSTNZH from three different sintering temperatures, namely, 1457, 1512, and 1567 K (in the temperature-AQ series samples), after 6 and 12 h of sintering at each temperature to preserve the high-temperature GB structures and prevent further microstructural evolution during slow cooling [43]. Previously, Ko *et al.* [33] suggested that Sr segregation and Nb substitution at GBs in air-quenched LSTNZH can contribute to increased B-site vacancies and GB structural disordering. Since the bimodal microstructures start to form at 1523 K in the furnace-cooled samples, we aim to quantify the bimodal structures in the

air-quenched samples and characterize the relationship between the GB structures and microstructural evolution.

The onset of the bimodal distribution of grain sizes starts at the intermediate temperature of 1512 K in the AQ series, where the second population appears above a grain size of 20 μm , as shown in Fig. 4(b). A pronounced separation of the small and large grain size populations is observed at 1512 K compared with the distribution at 1457 K. A sketch of a bimodal distribution function composed of two Gaussian distributions is presented in Fig. S16 in the ESM. The two populations are defined as normal distributions with means (μ) and standard deviations (σ) as follows: (μ_1, σ_1) = (6.58 μm , 4.41 μm) and (μ_2, σ_2) = (25.88 μm , 3.51 μm). At 1567 K, the two grain populations overlap and mix again, with a clear shift toward a large size. The largest grain size is approximately two times larger than that of the 1512 K sample. The tendency of the bimodal distribution of the three samples was subsequently quantified by the bimodality coefficient [85] described in Method (II) in the ESM. The results in Table S6 in the ESM demonstrate increasing bimodality as the temperature increases. Owing to the dramatic size difference between normal and abnormal grains, the average grain size typically lacks representation of entire microstructures. For comparison, the small and large grain populations were separated with the threshold $d_A/d_{\text{avg}} > 5$ [47], where d_A represents the grain size of abnormal grains (Fig. S17 in the ESM). The kinetic constants of normal grain growth (k_N) were first computed following cubic grain growth ($n = 3$), as shown in Eq. (1). The kinetic constants of abnormal grains (k_A) were subsequently calculated following Dillon and Harmer [73]:

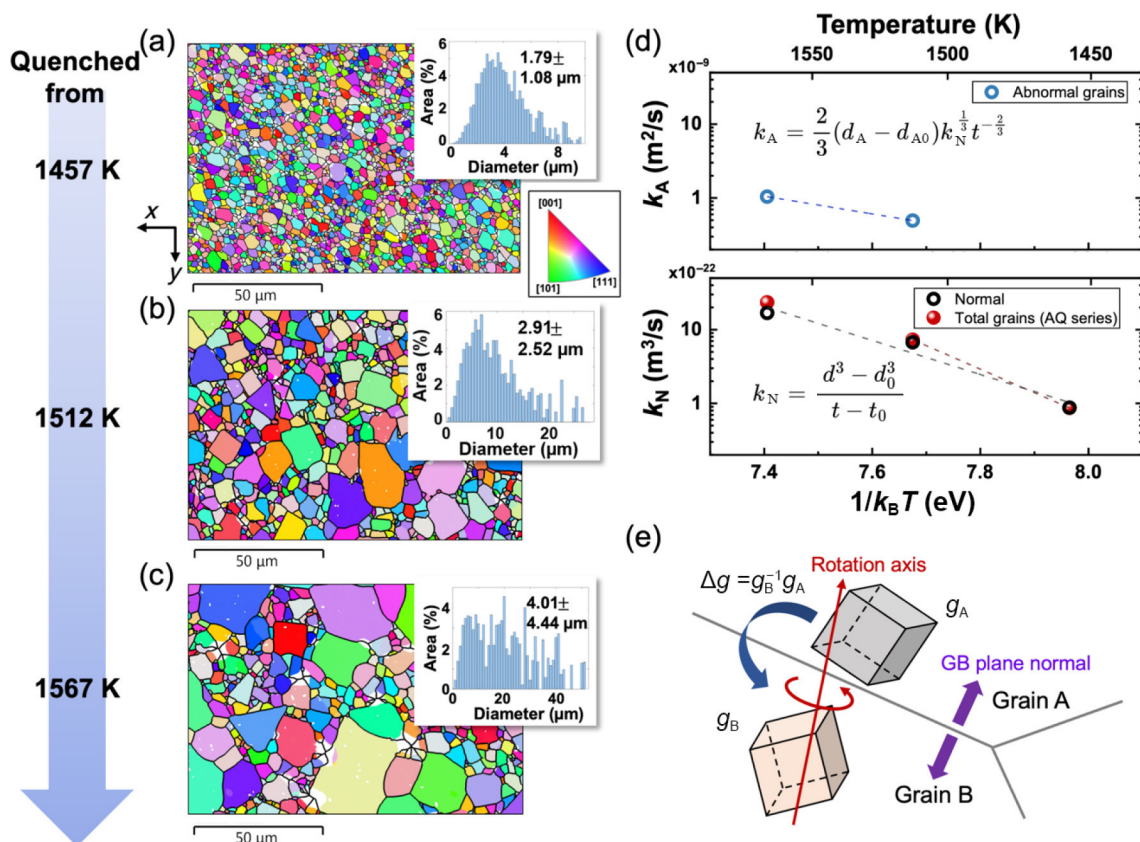


Fig. 4 (a–c) EBSD IPFs (normal direction) with area-weighted grain size distributions. (d) Temperature dependence of grain growth kinetics constants of total grains, normal grains, and abnormal grains of air-quenched samples. (e) Schematic illustration of five parameters of GB character. Here, rotation matrix, Δg , describes three degrees of freedom for misorientation between two grains. Orientation of grain boundary relative to one of the grains represents two other degrees of freedom. In panel (d), k_N and k_A refer to kinetic constants for normal and abnormal grain growth, respectively, whereas k_B is Boltzmann constant.

$$d_A - d_{A0} = \left(\frac{n}{n-1} \right) \frac{k_A}{(k_N)^{\frac{1}{n}}} t^{\left(\frac{n-1}{n} \right)} \quad (3)$$

where d_{A0} is the reference mean grain size of abnormal grains at 6 h. Figure 4(d) shows the temperature dependence of the kinetic constants of normal (k_N) and abnormal (k_A) grains. Considering the kinetic constants following the Arrhenius-type temperature-activated process, abnormal grains possess a much lower activation energy (2.77 eV) than normal grains do (5.31 eV) at 1512–1567 K, revealing a lower GB migration energy barrier for abnormal grains, presumably controlled by interfaces. The kinetic constant of total grains shows an increasing deviation from that of normal grains as the temperature increases, indicating that the average grain size becomes less representative for the calculations of the kinetic constant and activation energy at 1567 K, similar to the observation in the FC series in Fig. 3(b).

3.4 Temperature-induced transition in the GB character distribution

Given that grain growth is driven by the reduction in GB energy and that the growth rate is determined by the GB velocity, GB structures play a pivotal role in AGG [82]. To correlate AGG with the change in GB structure, we first investigated the effects of temperature on the crystallographic characteristics of the air-quenched samples. The GB velocity strongly correlates with five crystallographic parameters (macroscopic degrees of freedom) [86]. The five parameters that specify GB structures include the lattice misorientation (three parameters) and the GB plane inclination (two parameters), as schematically illustrated in Fig. 4(e) [87–90].

First, the misorientation angle describes the rotation angle relating two adjacent grains that is computed from their relative orientation difference [91–93]. A one-dimensional misorientation distribution function (MDF) represents the probability of the interfaces being a function of the rotation angle constructed by three-dimensional grain orientations, irrespective of the rotation axis. Figures S23(a)–S23(c) in the ESM show that the boundary MDF (experimental data) slightly deviates from the uniform and uncorrelated MDF curves for a nontextured cubic polycrystal proposed by Mackenzie [94]. Orientation correlations exist between neighboring grains but are independent of sintering temperature. A high multiple random density (MRD) value over 2 MRDs along [001] and a lower density along [011] at 1567 K reveal the existence of orientation anisotropy of neighboring grain pairs (Figs. S23(d)–S23(g)) in the ESM.

In addition, a GBPD analysis (Figs. S24–S26 in the ESM) revealed only a weak temperature dependence on preferential GB planes. A GB plane normal is defined as the normal vector of the interfaces by considering the facet plane of one grain as a reference. In Fig. S26(c) in the ESM, the higher frequency of the GB plane with a normal vector [001] is presented at 1457 and 1512 K, and the preferential GB plane normal changes toward $[\bar{1}11]$ at 1567 K. However, the MRD value differences between preferential and other random directions are not large compared with those of other materials (e.g., 0.6–1.8 MRD for STO; 0.8–1.225 for Y-doped alumina) [95,96]. The increase in the error bar at 1567 K is subject to local variations in the number of abnormal grains (Figs. S24–S26 in the ESM). Since the MRD value is inversely proportional to the GB energy [97,98], the gradient in the GBPD indicates the existence of GB energy anisotropy. A higher fraction of GBs oriented in {100} was observed by Rheinheimer *et al.* [95] in perovskite STO, which coincided with the presence of AGG. It can be deduced that the preferential GB plane and GB structure are developed as a

function of temperature driven by the reduction in the total interfacial energy. The GB energy is also a function of the misorientation that specifies interfaces [99]. We hypothesize that both the anisotropy of the misorientation axis distribution and the transition of the GB plane at 1567 K can be related to the change in GB structures with lower energy and greater mobility, which further results in AGG. Faryna *et al.* [100] also reported stronger anisotropy of GBPDs in YSZ as the grains became larger at higher sintering temperatures (1550 °C) with longer sintering times (20 h). However, large grain sizes are not sufficient conditions for strong anisotropy in both YSZ and STO, where GBPDs are indistinguishable in some samples, even those with various grain sizes [97,100]. The sintering conditions can play a key role in changing GB characteristics. To sinter compact equiaxed particles, GBPDs are presumably isotropic in the initial stage, and strong anisotropy can develop during grain growth by annihilating a fraction of high-energy GBs [97,101].

The distribution of GB types is also sensitive to GB segregation of impurities and the presence of 1–2 nm intergranular films in doped oxides [57,58,96,102]. For example, Ca-, Ba-, and Y-doped MgO exhibited a greater fraction of GBs in {100} plane than their undoped counterparts did, along with anisotropic segregation of Ca, Ba, and Y to GBs [102]. The anisotropy of GBPDs of Nd- and Ca-doped alumina increased after the temperature-dependent complexion transition, making them prone to AGG [103].

Next, we characterized the temperature-dependent GB segregation profiles of the quenched samples to obtain more direct evidence of a GB transition.

3.5 A temperature-induced GB transition

STEM-EDS was performed to characterize the elemental distribution across the GBs. Figures S27–S29 in the ESM display atomic-resolution HAADF images alongside EDS maps of the 1457 K (four GBs) and 1512 K (two GBs) samples. The grains aligned in the low-index zone axis show brighter contrast on the right or left grains in the HAADF images. From the intensity line profiles of the four GBs investigated in the 1457 K sample, we observe the uniform distribution of all the elements except Li, which is not detectable via EDS. In contrast, one of the GBs investigated in the 1512 K sample shows a slightly higher intensity of Nb (Fig. S29(b) in the ESM) from the lamella containing the GB between abnormal grains prepared by the FIB (Fig. S30 in the ESM). Combining the STEM-EDS results of the 1567 K air-quenched sample reported in our prior work [33], we evaluated the evolution of GB structures (Fig. 5), revealing temperature-dependent variations in GB segregation (i.e., adsorption via interfacial thermodynamics). The Gibbs GB excess [104], in units of atoms per area of GB, demonstrates increasing Nb segregation with increasing temperature.

Interestingly, the GB Nb segregation increases with increasing temperature, which contrasts with the classical Langmuir–McLean adsorption equation (Eq. (4)) [105,106]:

$$\frac{X_B^{GB}}{X_A^{GB}} = \frac{X_B^{Bulk}}{X_A^{Bulk}} \cdot e^{\frac{-\Delta g_{ads}^{B \rightarrow A}}{k_B T}} \quad (4)$$

where $\Delta g_{ads}^{B \rightarrow A}$ is the Gibbs free energy of GB adsorption (segregation) by swapping a B atom (cation) in the bulk phase with an A atom (cation) at the GB, X is the bulk or GB (denoted by the superscript) fraction of A or B (denoted by the subscript), k_B is the Boltzmann constant, and T is the absolute temperature. For a constant $\Delta g_{ads}^{B \rightarrow A}$, this equation is the Langmuir–McLean adsorption equation [105,106] for a fixed number of adsorption sites without considering the interactions of atoms at the GB

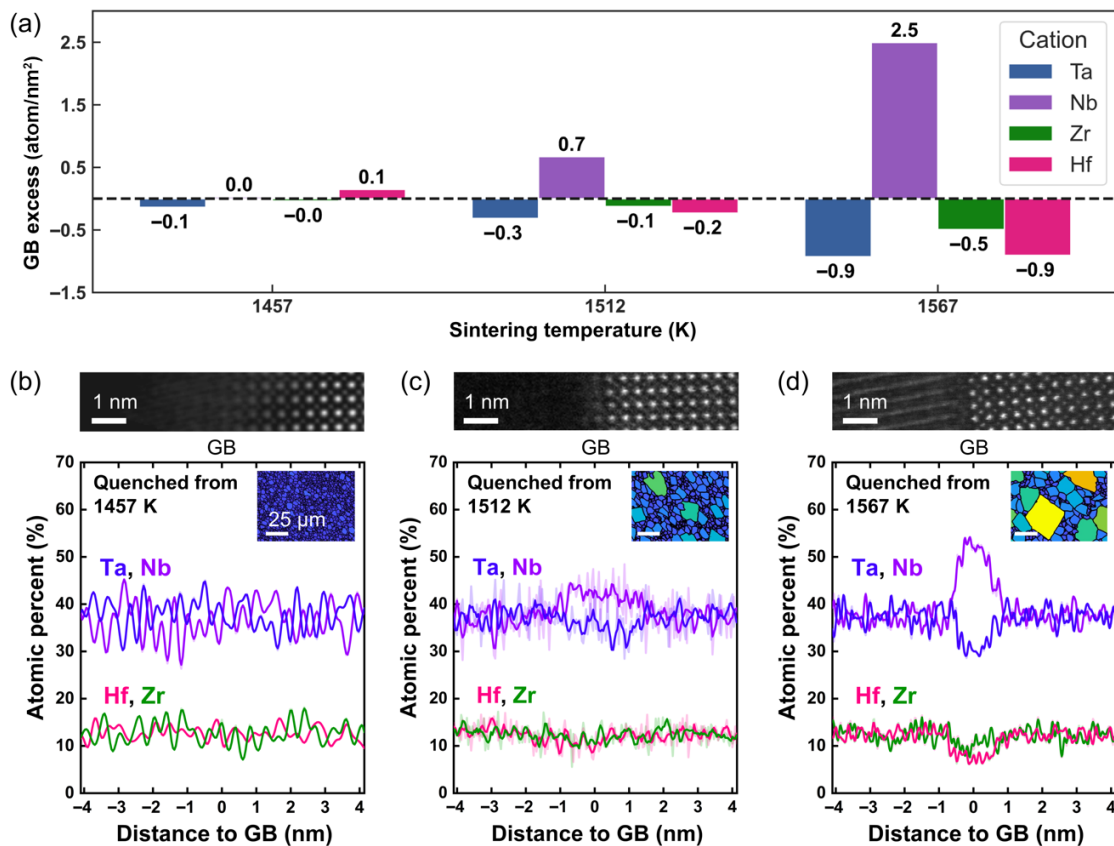


Fig. 5 (a) Comparison of GB excesses of B-site cations in LSTNZH quenched from 1457, 1512, and 1567 K. (b–d) Atomic resolution STEM-HAADF images and corresponding B-site elemental atomic percentage line profiles plotted against distance to GB. Raw profiles are displayed in a lighter color, whereas smoothed profiles are saturated color. Total atomic percentages of B-site cations are normalized to 100% at each position. Insets in (b–d) are EBSD grain maps color-coded according to grain diameter.

(treated as an ideal solution for simplicity), and it predicts decreasing GB adsorption with increasing temperature.

However, if temperature-induced GB disordering takes place, it can accommodate more adsorbates at the disordered (liquid-like) GBs at high temperatures in a coupled premelting and prewetting region, as discussed previously by Cannon *et al.* [107], modeled by Tang *et al.* [108] for a binary alloy, and elaborated by Luo [109,110]. This is consistent with the lower melting temperature of Nb_2O_5 (1512 °C) than those of Ta_2O_5 (1872 °C), ZrO_2 (2715 °C), and HfO_2 (2758 °C). Thus, GB segregation of Nb_2O_5 may promote the formation of liquid-like GBs, which in turn enhance the adsorption of Nb cations (in contrast to the temperature-induced desorption predicted by the classical GB segregation models of fixed GB adsorption sites). The observed temperature dependence of GB segregation of Nb supports the occurrence of GB disordering in a coupled premelting and prewetting region.

In general, observations suggest a GB complex (phase-like) transition [57]. In a broader context, GB segregation can induce phase-like GB structural transitions to form crystal-like, amorphous-like, or even quasicrystal-like 2D interfacial phases (complexions), which can possess distinct interfacial structures that influence kinetic, transport, and other properties [111]. For a complexion transition reported in Y-doped alumina, abrupt decreases in GB energy occurred, accompanied by the transformation of GB structures [112]. Segregation-induced premelting-like GB transitions were observed in ceramics [113,114] and refractory alloys [109,115], leading to the formation of liquid-like GBs, resulting in activated sintering. In our case, the temperature dependence of GB segregation of Nb (increasing with

temperature) is consistent with the occurrence of a GB premelting-like transition, which can be coupled with and enhanced by the segregation of low-melting Nb_2O_5 . Such a GB disordering transition can promote grain growth via enhanced transport kinetics at disordered GBs (akin to activated sintering promoted by liquid-like GBs [109,113–119]). However, the GBs observed at 1567 K in this case (Fig. 5(d)) are not “amorphous-like” (or liquid-like), as evident in previous reports of activated sintered ceramics [113,114] and refractory alloys [109,115]. It is possible that the GBs reordered during cooling (even with air quenching) from a high temperature (1567 K), similar to a prior case of activated sintered refractory high-entropy alloys [120].

For LSTNZH, moderate Nb enrichment coincides with the onset of exaggerated grain growth at 1512 K. The increase in GB excess of Nb becomes more pronounced at approximately 1567 K. Here, increasing GB segregation can be accommodated by temperature-induced GB disordering. The anisotropic occurrence of temperature-induced GB disordering can promote AGG and trigger bimodal microstructures due to the mixing of GB types with different mobilities [57,59–61].

Furthermore, the Nb-rich and Sr-deficient precipitates formed at elevated temperatures with longer sintering times (Figs. S16 and S17 in the ESM). When the sintering temperature increases (to 1623 K), Nb-rich and Sr-deficient precipitates form along GBs or at triple-grain junctions, indicating that the pseudopartial GBs are wetted with a dihedral angle $< 60^\circ$ [121]. A similar wetting layer has been found at GBs in Nb-containing Mg_3Sb_2 , accelerating grain growth [122]. Coupled GB premelting and prewetting have been suggested for Ni-activated sintered high-entropy alloy

MoNbTaW [120]. This study represents the first indication of such a GB disordering transition in CCCs or HECs. However, direct microscopy evidence of liquid-like (amorphous-like) GBs is absent for both cases, as the liquid-like GBs may have reordered (crystallized) during cooling.

Notably, the sluggish diffusion effect is not dominant when AGG occurs. Notably, this is not the only example of fast grain growth in HECs. Zhou *et al.* [123] reported the enhanced migration of GBs facilitated by oxygen vacancies in high-entropy rare-earth hexaaluminates. The presence of defects, such as vacancies, can also result in microstructural evolution. On the basis of the GB profiles in Fig. 5, the Nb substitution at the B sites suggests a greater net charge of B cations at the GBs, assuming that there are no B-site vacancies (Fig. S31 in the ESM). If the GBs remain largely ordered, there may be substantial B-site vacancies, the net charge of A-site cations may change, or space charges can form. However, the distribution of Li cannot be characterized by EDS, and the quenching effects (whether the high-temperature GBs are more disordered or even liquid-like) are unknown. Thus, the possible contributions from structural disordering vs. vacancies at the GB cores, as well as the possible occurrence and effects of space charges, are still inconclusive. Nonetheless, higher Nb segregation at higher temperatures and the occurrence of AGG suggest that GB disordering is coupled with segregation of the low-melting Nb_2O_5 component at high temperatures in a couple of GB premelting and prewetting regions [108,109,116].

In summary, we propose the occurrence of a temperature-

induced GB disordering transition that promotes GB segregation of Nb and grain growth with increasing temperature, which is consistent with prior observations of simpler materials [62,98,101,103,112,124–126], albeit with greater compositional complexity in CCCs. The occurrence of such a GB disordering transition, which takes place at different temperatures due to GB anisotropy in polycrystalline materials, can explain AGG and the formation of bimodal microstructures, in addition to the temperature-dependent GB segregation of Nb, which contradicts classical models.

3.6 Grain size effect on ionic conductivity and hardness

The influence of microstructure on ionic conductivity and hardness was also evaluated (Fig. 6 and Table 1). Figure S32 in the ESM shows the evolution of the impedance spectra with temperature for a fixed sintering time of 12 h. Even though both the bulk resistance ($> 10^7$ Hz) and the GB resistance (10^6 – 10^7 Hz) decrease as the sintering temperature increases from 1473 to 1573 K, the reduction in the GB resistance is more pronounced than the change in the bulk resistance with increasing grain size. The changes in the apparent GB ionic conductivities (σ_{GB}) shown in Fig. 6(a) align with the changes in the mean grain sizes shown in Fig. 3(c). The highest σ_{GB} at 1573 K is attributed to the largest mean grain size (with the lowest effective volume fraction of GBs). The total ionic conductivity (σ_{total}) as a function of sintering temperature demonstrates a consistently increasing trend as that of σ_{GB} from 1473 to 1573 K, as the increase in the bulk ionic

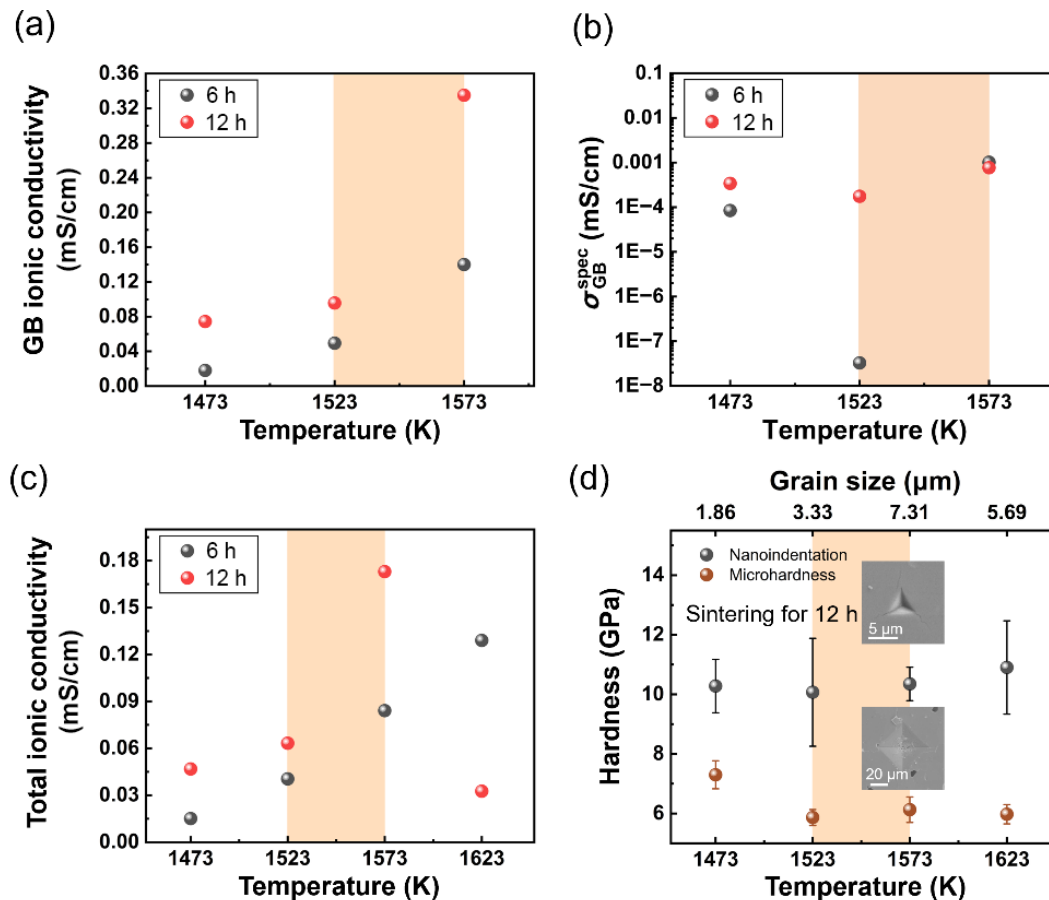


Fig. 6 (a) Apparent GB ionic conductivity, (b) specific GB ionic conductivity, (c) total ionic conductivity, and (d) Vickers microhardness (brown dots) and nanoindentation (gray dots) measurements. The error bars in (d) represent ± 1 SD, indicating uncertainty in the measurements. Insets in (d) display secondary electron images of nanoindent (upper) and diamond-shaped microindent (lower). Orange shaded areas represent temperature window associated with bimodal microstructures due to AGG.

conductivity (Fig. S33 in the ESM) has less of an impact on σ_{total} . The decrease in σ_{total} at 1623 K can be attributed to the formation of crystalline LiNbO_3 precipitates at the GBs, which have a low Li-ion conductivity on the order of 10^{-11} S/cm [127]. According to the brick layer model, the specific (true) GB ionic conductivity ($\sigma_{\text{GB}}^{\text{spec}}$) equals σ_{GB} multiplied by the ratio of the bulk capacitance to the GB capacitance [78]. For the 12 h series, an increase in $\sigma_{\text{GB}}^{\text{spec}}$ is observed for the 1573 K sample (7.67×10^{-7} S/cm), which is greater than that of the 1473 K sample (3.39×10^{-7} S/cm). Notably, this comparison of $\sigma_{\text{GB}}^{\text{spec}}$ is based on furnace cooling samples, where GB segregation was not reported in prior studies [33]. The ionic conductivities (σ_{GB} and σ_{total}) may depend on both the microstructure (grain size) and actual GB structure.

In addition to ionic conductivity, hardness is also a microstructure-dependent property [128]. We conducted Vickers hardness tests and nanoindentation tests on samples sintered from 1473 to 1623 K for 12 h to investigate the effect of the grain size on hardness. The classic Hall-Petch relationship depicts the GB strengthening effect as the grain size decreases. This relationship has been studied in LLZO and other ceramic systems [129,130]. In Fig. 6(c), the decrease in the Vickers microhardness as the mean grain size increases is notable for the samples sintered from 1473 to 1573 K, and the hardness does not increase again despite the decrease in the grain size at 1623 K. In contrast, the hardness values from the nanoindentation test are independent of the grain size, which has been observed in other ceramic materials [131]. The difference between the two tests is the size of the indent. The insets in Fig. 6(c) display images of the indents of the microhardness and nanoindentation tests. The nanoindent size is similar to or smaller than the grain size, so each nanoindent captures only the mechanical strength of a single grain or a single GB. According to Nakamura *et al.* [132], the hardness at grain interiors and near single GBs shows negligible differences in YSZ, STO, and Al_2O_3 . Although GBs act as barriers to dislocation motion, the overall strengthening effect of GBs in oxides is less significant than that in metals. Likewise, the microhardness becomes independent of the mean grain size and relative density above 1523 K upon exaggerated grain growth. It is likely that the micro indentations are located in grains larger than the indent size and capture hardness from only a few grains. Thus, the grain size effect becomes negligible. The hardness of LSTNZH sintered at 1473 K is comparable (7.30 ± 0.48 GPa) and falls within the typical hardness range of OSEs, such as $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ and garnet-type LLZO (5–10 GPa), as measured in microhardness tests [8,10,11,129,133].

4 Conclusions

We investigated the temperature-dependent microstructural evolution of the medium-entropy CCPO LSTNZH. At moderate temperatures, grain growth follows the classical cube-root time dependence. As the sintering temperature increased, abnormal grain growth or AGG occurred in the intermediate temperature range (1523–1573 K). At 1623 K, the grain size distribution becomes normal again because of the impingement effect between large abnormal grains. The change in the GB character distribution with temperature has been characterized, which suggests a possible occurrence of a GB transition.

Furthermore, we discovered increasing GB segregation of Nb with increasing temperature, which coincides with the onset of AGG. This temperature-induced GB segregation transition contrasts with the classical GB segregation models that predict desorption (desegregation) with increasing temperature, but it can be explained by temperature-induced GB disordering (akin to GB

premelting). Such a GB disordering transition and its anisotropic occurrence can explain AGG and the formation of bimodal microstructures. The increased grain growth improved the total ionic conductivity.

This work represents the first in-depth study of temperature-dependent microstructural evolution and AGG in CCCs and HECs, and it provides new insights into the fundamental understanding of grain growth phenomena and mechanisms in CCCs and HECs.

Acknowledgements

This research was primarily supported by the National Science Foundation (NSF) Materials Research Science and Engineering Center (MRSEC) program through the UC Irvine Center for Complex and Active Materials (CCAM) under No. DMR-2011967. This work used shared facilities at the Irvine Materials Research Institute (also supported in part by the NSF DMR-2011967), the San Diego Nanotechnology Infrastructure (SDNI) of UCSD, a member of the National Nanotechnology Coordinated Infrastructure (NSF ECCS-2025752), the NSF Center for Chemistry at the Space-Time Limit (CHE-0802913), the UC San Diego MRSEC shared instrumentation (NSF Grant DMR-2011924), and the UC San Diego Nanoengineering Materials Research Center (NE-MRC).

Author contributions

Jian Luo and Shu-Ting Ko conceived the study and designed the experiments. Jian Luo and Xiaoqing Pan supervised different aspects of the project. Shu-Ting Ko conducted the material synthesis, XRD, TGA/DSC, EBSD, SEM, microhardness tests, and most of the data analysis. Tom Lee, Huiming Guo, Jenna L. Wardini, and Shu-Ting Ko performed the TEM sample preparation, which was supervised by William J. Bowman. Chaojie Du and Tom Lee conducted STEM and data analysis with the help of Francisco Guzman. Hasti Vahidi carried out the *in situ* XRD. Tom Lee measured ionic conductivities. Jingjing Yang and Shu-Ting Ko carried out the SEM-EDS characterization. Yi Liu performed nanoindentation, which was supervised by Timothy J. Rupert. Shen J. Dillon provided suggestions on the initial draft and EBSD analysis. Shu-Ting Ko wrote the initial draft, and Jian Luo revised and finalized the manuscript. All the authors contributed to the discussion and revision of the manuscript.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article. The author Jian Luo is the Editorial Committee member of this journal.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.26599/JAC.2025.9221047>.

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