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# Elastic properties of Sr- and Mg-doped lanthanum gallate at elevated temperature

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**Abstract**

The elastic moduli, i.e., Young's modulus, shear modulus and Poisson's ratio, of a sintered $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ bulk have been experimentally determined in the temperature range from room temperature to 1373 K using a resonance technique. Anomalous elastic properties were observed over a wide temperature range from 473 to 1173 K. In the results for internal friction and in X-ray diffraction measurements at elevated temperature, two varieties of structural changes were seen in $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ in the examined temperature range. The results agreed with the findings of a previous crystallographic study of the same composition system by Slater et al. In addition, the temperature range in which a successive structural change occurred in $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ was the same as that exhibiting the anomalous elastic properties. Taking all the results together, it can be inferred that the successive structural change in the significant temperature range is responsible for the elastic property anomaly of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$.


*Keywords:* LSGM; Elastic modulus; Internal friction; X-ray diffraction; Structural change

## 1. Introduction

Sr- and Mg-doped lanthanum gallate (LSGM) has been looked to as a new electrolyte material for the solid oxide fuel cell (SOFC) because of its excellent oxide-ion conductivity [1]. For that reason, an LSGM electrolyte has been extensively studied in recent years for application to the SOFC and there are several reports about its performance in the literature [2,3]. It is known that the SOFC with an LSGM electrolyte can effectively operate at high temperatures of more than 900 K. For practical applications of the SOFC with an LSGM electrolyte, the device must survive consecutive operation for thousands of hours in an elevated temperature range. In addition, it must also be able to withstand thermal stress caused by the resulting temperature gradient and the incompatibility of the thermal expansion between the electrolyte and the bilateral electrodes in the heating or cooling process because the SOFC often experiences a cyclic temperature history at startup and shutdown. For such reasons, it is absolutely essential to verify the mechanical properties of the LSGM electrolyte at elevated temperatures to facilitate practical applications of the SOFC with this electrolyte. However, there have been few reports so far about the mechanical properties of LSGM at high temperature. In this study, we have investigated the temperature dependence of the principal elastic moduli, i.e., Young's modulus, shear modulus and Poisson's ratio, of a sintered LSGM bulk because the elastic moduli are among the most significant and fundamental parameters of mechanical properties in materials. This paper presents the elastic moduli of the LSGM bulk at various elevated temperatures and describes their anomalous temperature dependence.

## 2. Experimental procedures

In this study, the LSGM bulk selected for investigation of its elastic properties was $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$, which has been identified by Ishihara et al. [1]. Powder having a mean grain size of 0.68 μm (D50) was purchased from SEIMI CHEMICAL Co., Ltd. for use in fabricating the LSGM bulk. The LSGM bulk was prepared by pressureless sintering at 1723 K in the air for 6 h. X-ray powder diffraction (XRD) measurements were performed on the LSGM bulk at room temperature (RT) to confirm that it consisted of the single perovskite phase. In addition, XRD measurements were also performed at high temperatures up to 1373 K in

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order to confirm whether crystallographic changes occurred or not in the examined temperature range in the LSGM bulk because such structural changes often cause elastic property anomalies. A resonance technique was used to measure each elastic modulus of the LSGM bulk at high temperature. The shape of the specimen for the resonance tests was a rectangular plate, measuring 40 mm × 15 mm × 1 mm. The specimen was suspended by two alumina fibers in the furnace. The fibers were connected to a speaker and a pick-up sensor, respectively. One fiber transferred vibrations from the speaker to the specimen and the other carried the resonant vibrations resulting in the sample to the pick-up sensor. Each elastic modulus was estimated from a detected primary resonance by using the following appropriate ways. Young's modulus was evaluated in the temperature range between RT and 1373 K in 100 K increments by the Japanese Industrial Standard (JIS) test method using the flexural mode of the resonance frequency [4]. The shear modulus was evaluated in the same temperature range by the standard test method of the American Society for Testing and Materials (ASTM) using the torsional mode [5]. Poisson's ratio was calculated by the prevailing method, assuming a homogeneous and iso-elastic body and using the measured elastic moduli. Internal friction was also measured in parallel with Young's modulus. It is sensitive to structural changes like phase transitions which are frequently observed in perovskite phases. Such structural changes should cause significant variation in the elastic properties of materials and, therefore, internal friction is often used as a criterion to substantiate the variation in the elastic moduli [6–10].

## 3. Results

Fig. 1 shows the XRD profile for the selected LSGM bulk at room temperature. In this figure, the diffracting plane indices on the peaks are expressed as the orthorhombic symmetry (Pbnm) because the no-doped $LaGaO_3$ perovskite phase was identified as the orthorhombic one at room temperature by Marti et al. [11]. As shown in Fig. 1, this profile consisted nearly entirely of the peaks attributed to $LaGaO_3$ perovskite phase, which suggests that the Sr and Mg dopants were successfully substituted in $LaGaO_3$. Any further discussion about the crystallography of the LSGM bulk was not attempted here because this treatment is sufficient for judging only whether the principal constituting phase is $LaGaO_3$ perovskite phase or not. Fig. 2 shows the variation in Young's modulus for the LSGM bulk at the elevated temperatures up to 1373 K. In this figure, the open circles show the Young's modulus of the LSGM bulk with increasing temperature. It should be noted that the Young's modulus displayed anomalous behavior over an exceptionally wide temperature range from 473 to 1173 K. More specifically, it rapidly decreased in the temperature range from 473 to 873 K, then antithetically increased in the temperature range from 873 to 1173 K, and finally decreased again. This unique Young's modulus behavior was reproduced in tests conducted several times. Fig. 3 shows the temperature dependence of the shear modulus and Poisson's ratio for the LSGM bulk, and Table 1 gives all the evaluated values in Figs. 2 and 3. As can be seen in these results, the shear modulus also exhibited the same behavior as Young's modulus, and Poisson's ratio displayed a visible variation around 873 K. In familiar materials, Young's modulus and the shear modulus tend to decrease monotonously with increasing temperature, as depicted by the dashed line in Fig. 2, and Poisson's ratio should remain constant. As will be described later, it can be understood that these variations in the elastic moduli resulted from a successive structural change of the LSGM bulk in the immediate temperature range. Fig. 4 shows the temperature dependence of the internal friction of the LSGM bulk. In familiar materials, it should increase monotonously and gradually with increasing temperature, as depicted by the dashed line in Fig. 4, so long as there are no

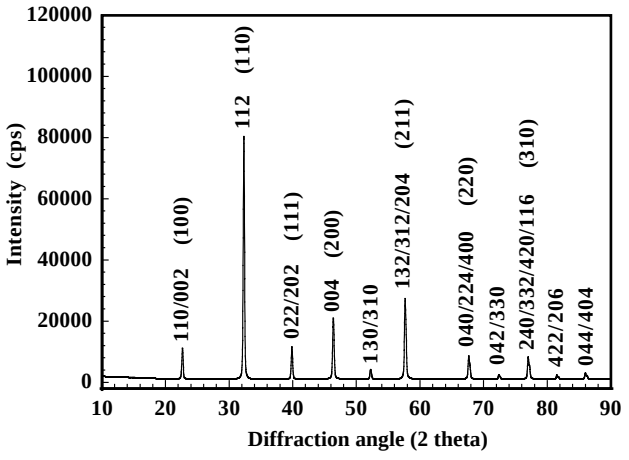


Fig. 1. XRD profile of as-sintered LSGM bulk at room temperature. Indices on diffraction peaks are expressed for orthorhombic symmetry and those in parenthesis are for quasi-cubic.

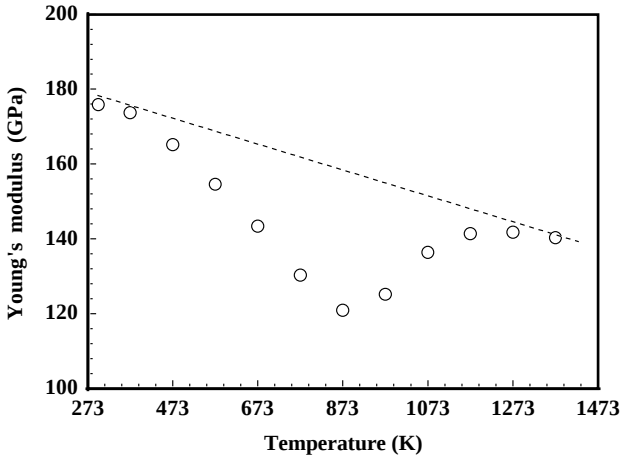


Fig. 2. Variation of Young's modulus of LSGM bulk in the temperature range between RT and 1373 K.

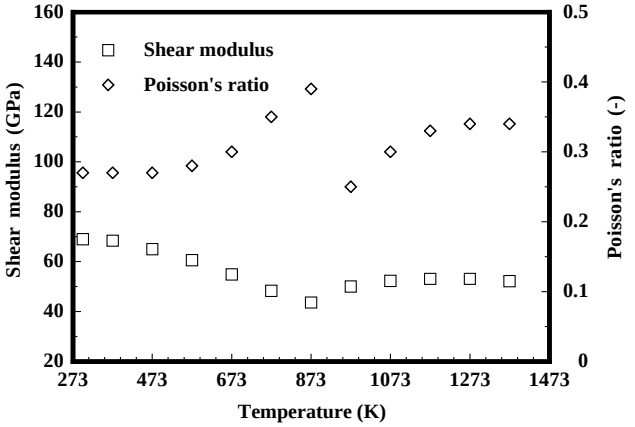


Fig. 3. Other elastic moduli of LSGM bulk in the temperature range between RT and 1373 K. Open squares and rhombuses show shear modulus and Poisson's ratio with increasing temperature, respectively.

Table 1
Elastic properties of LSGM bulk in the temperature range between RT and 1373 K

| Temperature (K) | Young's modulus (GPa) | Shear modulus (GPa) | Poisson's ratio |
|---|---|---|---|
| RT | 176 | 69.0 | 0.27 |
| 373 | 174 | 68.4 | 0.27 |
| 473 | 165 | 65.0 | 0.28 |
| 573 | 155 | 60.6 | 0.30 |
| 673 | 142 | 54.9 | 0.35 |
| 773 | 130 | 48.3 | 0.39 |
| 873 | 121 | 43.6 | 0.25 |
| 973 | 125 | 50.0 | 0.30 |
| 1073 | 136 | 52.3 | 0.33 |
| 1173 | 141 | 53.1 | 0.34 |
| 1273 | 142 | 53.1 | 0.34 |
| 1373 | 140 | 52.2 | 0.34 |

internal (i.e., crystallographic or microstructural) changes in the materials. In this figure, however, the scattergram exhibits two visible peaks as indicated by the arrows; one is at about 473 K and the other is at about 773 K. In addition, relatively high internal friction values were observed in the

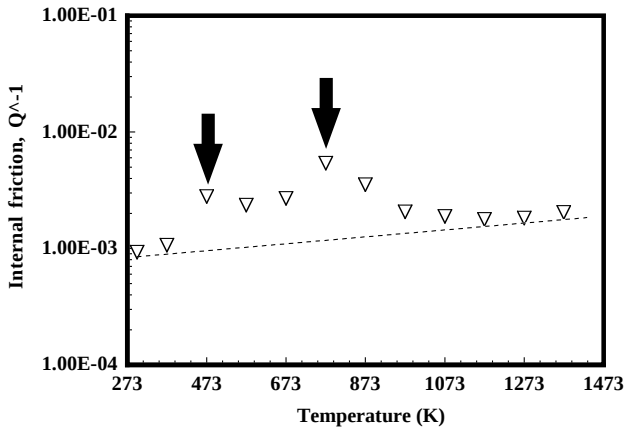


Fig. 4. Variation of Internal friction of LSGM bulk in the temperature range between RT and 1373 K.

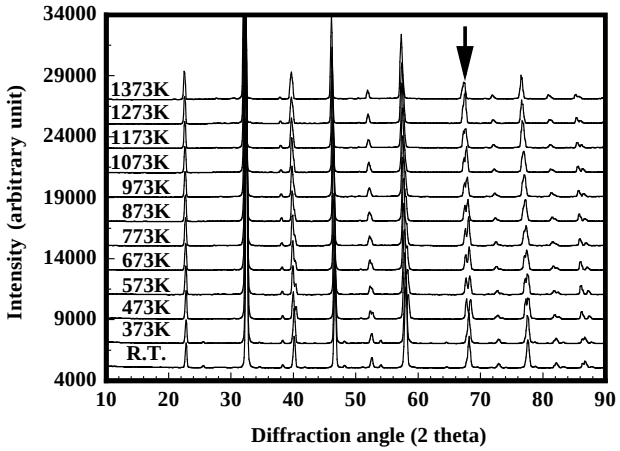


Fig. 5. Variation of XRD profiles for LSGM bulk in the temperature range between RT and 1373 K.

temperature range between 473 and 1173 K. As will be seen later, these specific temperatures approximately correspond to those of the two varieties of structural changes identified previously for the same composition system by Slater et al. [12], respectively. Furthermore, the significant temperature range corresponded almost completely to that in which the elastic property anomaly of the LSGM bulk was observed. Fig. 5 shows the variation of the XRD profiles for the LSGM bulk in the temperature range from RT to 1373 K. This series of XRD profiles suggests that the LSGM bulk maintained the $LaGaO_3$ perovskite phase over the whole temperature range, with the peaks slightly shifting to lower diffraction angles with increasing temperature. Upon closer inspection, however, two characteristic changes were found in the profiles. Firstly, the peaks of 040/224/400, as indicated by the arrow, and some higher order plane indices split dramatically into two in the temperature range between 373 and 473 K. Secondly, the relative intensity ratio between the split peaks varied gradually in the temperature range from 473 to 1173 K. As will be seen later, it is known that the former variation between 373 and 473 K is attributed to the structural change from orthorhombic to rhombohedral symmetry and the latter variation from 473 to 1173 K was attributed to the successive structural change that maintained the rhombohedral symmetry. The anomalous elastic properties of the LSGM bulk were identified in the latter temperature range. From the consistency between our results and the previous findings, therefore, it can be inferred that the successive structural change in the intermediate temperature range was responsible for the elastic property anomaly of the LSGM bulk.

## 4. Discussions

An elastic property anomaly was observed for the LSGM bulk over the wide temperature range from 473 to 1173 K in this study. As described in the previous section, the LSGM bulk displayed two varieties of structural changes in the

examined temperature range and its elastic property anomaly should be related to the successive structural change in the intermediate temperature range. The "two" specific structural changes in the LSGM were first reported by Slater et al. [12] using a neutron diffraction technique. They reported that the crystal structure of the LSGM was transformed from pseudo-orthorhombic to pseudo-rhombohedral at a temperature between 523 and 773 K, and was further transformed to rhombohedral (R3c) at a temperature between 773 and 1023 K. They also mentioned that the former structural change was a first-order phase transition and the latter was a second-order phase transition. Our results coincided with their findings. A local minimum of elastic moduli with increasing or decreasing temperature is often observed in materials undergoing phase transitions and has been reported for many materials so far [6–10]. The reason is physically understandable as such structural change is probably accompanied by phonon softening in the vicinity of the Γ-point in reciprocal space ($k = 0$) and renders the specific elastic constants close to zero. As a result, the elastic moduli of such materials would show anomalous behavior during the structural change. For that reason, an elastic property anomaly should be more distinctly observed when the structural change is not dramatic but consecutive. The elastic property anomaly of the LSGM bulk was visibly observed in the temperature range in which the successive structural change occurred. This indicates that the successive structural change would also occur with the phonon softening over the temperature range from 473 to 1173 K in the LSGM bulk. In other words, the elastic property anomaly suggests that the significant structural change was occurring throughout the intermediate temperature range. It would seem to be somewhat questionable that the temperature range with the significant structural change is completely true, because the range is too wide for that of the structural change. In doped ionic materials, in general, structural changes such as lattice distortion, which is similar to a second-order phase transition, can occur easily because a number of vacancies are doped in the crystal. In high ion-conducting materials such as LSGM, in particular, the trend would be more pronounced. Therefore, there is a good possibility that an auxiliary structural change could also occur at high temperature. That is to say, the elastic property anomaly of the LSGM bulk may be affected not only by the second-order phase transition indicated by Slater et al., but also by the auxiliary structural change. At present, the details of the significant structural change in the LSGM are open to question, but its occurrence should be taken seriously. Our results suggest a fundamental problem for applications of LSGM. This unique elastic property could be an advantage for thermal shock resistance, but also a disadvantage as far as the incompatibility of thermal expansion is concerned, because an anomalous thermal expansion would also frequently be present when an elastic property anomaly appeared in materials. Our study cautions that we must consider elastic properties in combination with electric properties for facilitating practical application of the SOFC with the LSGM electrolyte.

## 5. Summary

The principal elastic moduli of LSGM were experimentally determined in the temperature range between RT and 1373 K using a resonance technique. As a result, anomalous elastic properties of the LSGM bulk were identified in the temperature range from 473 to 1173 K. In the results for internal friction and in X-ray diffraction measurements at elevated temperature, a successive structural change was seen in the same temperature range as that showing the anomalous elastic properties of the LSGM bulk. These results suggest that the structural change in the immediate temperature range was closely related to the elastic property anomaly of the LSGM bulk.

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