Effect of excess lithium on the electrical properties of $Li_{0.25}La_{0.25}NbO_3$ ceramics

SHIHANG HU[1], SHUAI ZHANG[1], CHENGCHENG CAI[1], ZEXIONG WANG[1], JIE CHANG[1],
YAZHOU KONG[1,*], HONGBO WANG[2], KAILONG ZHANG[3], GUANG HU[1], WEIWEI HU[1], HAO SUN[1],
JINQUAN WANG[1], JIADONG ZHANG[1], KUN HONG[1]
[1]National & Local Joint Engineering Research Center for Mineral Salt Deep Utilization, Faculty of Chemical
Engineering, Huaiyin Institute of Technology, Huaian 223003, P. R. China
[2]Jiangsu Oseaguard Science and Technology Co., Ltd, Huaian 223100, P. R. China
[3]Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, Huaian 223003, P. R. China

In this study, the effect of excess Li_2CO_3 in raw materials on the electrical property for $Li_{0.25}La_{0.25}NbO_3$ ceramic has been researched. $Li_{0.25}La_{0.25}NbO_3$ solid electrolytes with different contents of excess Li_2CO_3 was prepared via a simple solid state reaction. The conductivity of LLNO-Li 15 (15 wt % excess Li_2CO_3) is 1.17×10^{-5} S cm^{-1} at 25 °C, which is 100 times higher than that of LLNO-Li 0 without excess Li_2CO_3. An appropriate proportion of excess Li_2CO_3 significantly improves the conductivity of LLNO ceramics. However, over numerous excess lithium will also damage the conductivity. The optimal excess lithium content is determined to be 15 wt%.

1. Introduction

New energy batteries, such as solar cells [1] and secondary batteries, are related to the sustainable development of human society and have received increasing attention. $Li_{0.25}La_{0.25}NbO_3$ (LLNO) and related compounds are considered as potential solid electrolytes for all solid state lithium secondary batteries. LLNO exhibits the A-site-deficient perovskite structure [2] with high intrinsic vacancies [3] concentration. Several advantages can be found in LLZO system, such as low sintering temperature [3, 4] and large lattice volume [2, 3, 6]. The reported highest grain conductivity of LLNO is about 10^{-4} S cm^{-1} [7], while its total conductivity is only 10^{-5} S cm^{-1} at room temperature [8]. Kawahara et al. [9] found that grain boundary ionic conductivity of LLNO is 3-times higher than bulk conductivity, which differs from LLTO and other oxide type solid electrolyte system.

Many works have been reported to improve the conductivity of LLNO. Cation substitution has a significant impact on the structure and properties of ceramics [10]. Yang et al. [11] synthesized $Li_yLa_{(1-y)/3)1-x}Sr_{0.5x}NbO_3$ by co-doping Li^+ and Sr^{2+} into LLNO. $(Li_{0.1}La_{0.3})_{0.92}Sr_{0.04}NbO_3$ exhibits a high total conductivity of 8.002×10^{-5} S cm^{-1} at room temperature. Zheng et al. [4] reported that Sr^{2+} ions doping expanded the perovskite unite cell volume and improved the conductivity of LLNO ceramic. However, the conductivity of LLNO is still far from the requirements of solid-state batteries worked at room temperature.

The preparation process of materials has huge influence on the conductivity of ceramics. The sintering temperature for LLNO ceramic is 1100 °C. Lithium carbonate and lithium hydroxide are often used as raw materials to prepare LLNO. These lithium-containing compounds always evaporate at high temperature. The evaporation of lithium-containing compounds can influence the crystal structure, change the chemical composition and reduce the total conductivity of LLNO solid electrolyte. Adding additional lithium-containing compounds to raw materials is a universal way to reduce the impact of lithium volatilization loss [12–14], which can be considered as a low-cost and easy-operating approach in the large-scale industrial production processes for LLNO ceramics. The appropriate content of excess-lithium will be an important parameter for large-scale industrial production of LLNO solid electrolytes.

$Li_{0.25}La_{0.25}NbO_3$-based ceramics are potential candidates that can be used as solid electrolytes for high-performance all-solid-state lithium-ion batteries. The processing of LLNO ceramics requires high temperature sintering, leading to volatilization loss of lithium. During the preparation of lithium-containing ceramics, excess Li_2CO_3 or LiOH is usually added into raw materials to balance the volatilization loss and improve the ceramic property. The appropriate content of excess Li_2CO_3 plays an important role during large-scale industrial production of LLNO solid electrolytes. In this paper, we prepared LLNO ceramic solid electrolytes with different proportion of excess Li_2CO_3 contents in the precursor materials by solid state reaction method. We used Li_2CO_3 as an excess lithium-source and studied the influence of excess Li_2CO_3 in raw materials on the structure and electrical property of

$Li_{0.25}La_{0.25}NbO_3$ ceramic.

2. Experimental

$Li_{0.25}La_{0.25}NbO_3$ ceramics with different excess lithium carbonate contents in raw materials were prepared by the solid state reaction method. The raw materials La_2O_3 (99.9 %), Li_2CO_3 (99.8 %) and Nb_2O_5 (99.5 %) were weighed based on the stoichiometry of $Li_{0.25}La_{0.25}NbO_3$. The excess lithium carbonate contents were 0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% and 25 wt%, respectively. The ceramic samples were named as LLNO-Li 0, LLNO-Li 5, LLNO-Li 10, LLNO-Li 15, LLNO-Li 20 and LLNO-Li 25, respectively. All ingredients were mixed by using ball milling for 4 h with the speed of 250 rpm min^{-1}. Alcohol (AR, 99.7%) was used as a medium during the ball milling process. After ball-milling, the mixed powder was calcined at 900 °C in air for 12 h. Then the calcined powder was reground to obtain uniform powder size. Ceramic pellets were formed by pressing the calcined powder in a 15 mm diameter die. Ceramic pellets were pressed at 10 MPa for 1 min. Finally, all samples were sintered at 1100 °C for 12 h in a muffle furnace and quenched in air.

After the sintering process, all samples were polished with 400, 800, and 1200 mesh sandpaper before all the characterizations. Phase purity and crystal structure of sintered ceramic pellets were confirmed using a Bruker D8 X-ray Diffractometer (XRD, 15-80˚). Porosity, grain size and fracture-face microstructure of samples were examined on photographs collected using S-3000N (SEM) equipment. Ceramic pellets were carried out thermal corrosion before SEM test. Before property characterizations, the surface of ceramic pellets was sprayed with Ag electrode paste and dried in a furnace at 150 °C, and then the Ag-based ionic blocking electrode was obtained. The conductivity of samples was determined by AC impedance spectra with a frequency region from 1 to 10000000 Hz using CHI660E equipment. The AC impedance spectra were practiced at different temperatures from 25 to 100 °C to identify the activation energy of each sample. The electronic conductivity of all ceramic samples was measured by DC polarization measurement with a constant applied voltage of 2 V and a duration time of 6000 s at 25 °C.

3. Results and discussion

The XRD spectra of ceramic pellets are shown in Fig. 1. For the synthesized ceramic sample without excess Li_2CO_3, the main phase corresponds to perovskite structure, but some peaks belonging to the Nb_2O_5 impurity phase were observed. For the sample with 25% excess Li_2CO_3, the main phase also corresponds to perovskite structure, but Nb_2O_5 and $LiNbO_3$ impurities were observed. Other ceramic samples also show perovskite structure, while some impurities peaks of other materials were observed in the range of 2 theta = 25° to 28°. With the

increase of excess lithium, the main peak of samples shifts to the right region gradually, but the main peaks of LLNO-Li 25 shifted toward lower angles compared to the other samples. The radius of lithium ion is smaller than that of lanthanum ion. Lithium ions are constantly entering the A site of perovskite. But excessive Li content led to the production of Nb_2O_5 and $LiNbO_3$ impurities. So, adding 15-20 wt% lithium carbonate in raw materials is an effectively way to produce well-crystallized LLNO solid electrolyte ceramics.
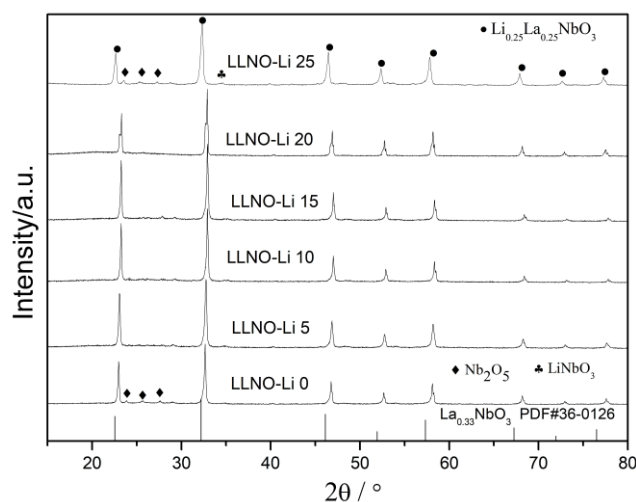

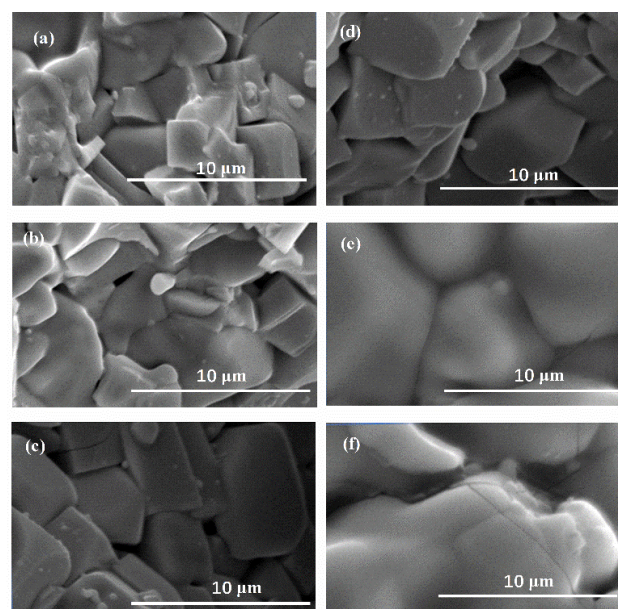*Fig. 1. XRD result of ceramic pellets sintered at 1100 °C*

Fig. 2. SEM images of the cross-sectional area of the ceramic pellets, (a) LLNO-Li 0, (b) LLNO-Li 5, (c) LLNO-Li 10, (d) LLNO-Li 15, (e) LLNO-Li 20 and (f) LLNO-Li 25

The fracture microstructure images of ceramic samples are shown in Fig. 2. The grain size of each sample is approximately 3-8 μm. Pores can be observed in Fig. 2. The samples of LLNO-Li 10, LLNO-Li 15 and LLNO-Li

20 have fewer holes with a homogeneous morphology and better fusion between each grain. It can be observed that something seems like it melts and connects grains. Some wrinkles can be observed, which is caused by thermal stress generated by quenching. With regard to the sample of LLNO-Li 25, cracks appeared with a rough appearance, which is considered to be detrimental to lithium transportation. An appropriate proportion of excess lithium may be beneficial to improve the microstructure and the grains' growth.
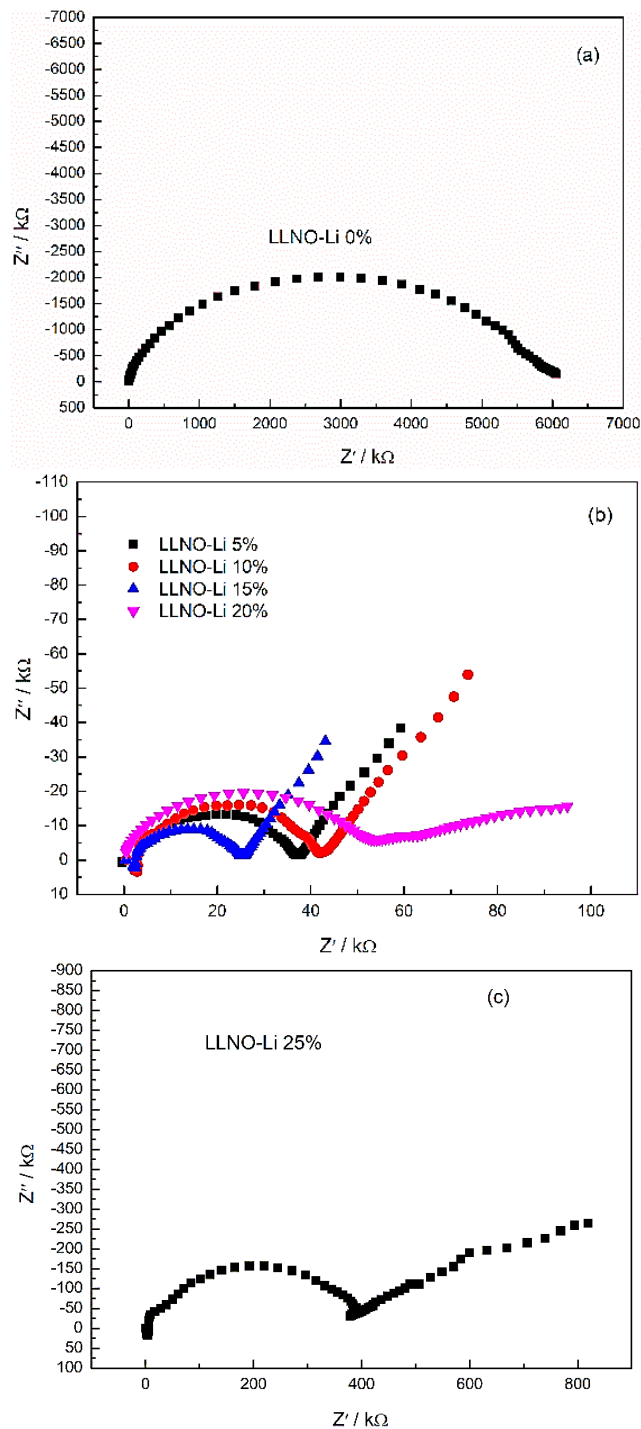

Fig. 3. Nyquist plot of ceramic pellets, (a) LLNO-Li 0, (b) LLNO-Li 5, LLNO-Li 10, LLNO-Li 15, LLNO-Li 20 and (c) LLNO-Li 25 (color online)

The AC-impedance plots of samples are shown in Fig. 3. The Nyquist plot of ceramic pellets was fitted by Zsimpwin. The conductivity of LLNO-Li 0 is 4.93×10^{-8} S cm^{-1}, which is extremely low for application as a solid electrolyte. Therefore, it is necessary to add excess lithium in raw materials for LLNO ceramic to balance the evaporation of lithium during high temperature sintering. The conductivity of samples was increased by increasing the excessive amount of Li_2CO_3, reaching a maximum value of 1.17×10^{-5} S cm^{-1} at 15 wt% excess Li_2CO_3. Further addition of excess Li_2CO_3 deteriorated the performance of conductivity. The conductivity of LLNO-Li 25 is only 7.48×10^{-7} S cm^{-1}. An appropriate amount of excess lithium significantly improves the conductivity of LLNO ceramics. However, the excess lithium will damage the conductivity property of electrolyte. From the perspective of enhancing conductivity, the optimum excess lithium content is 15 wt%.

Table 1 Conductivity and activation energy of ceramic samples

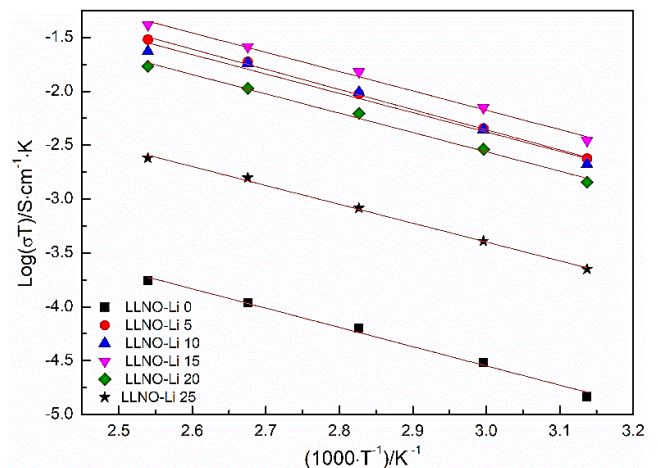| Sample	$\sigma_{total}/25\,°C$	Ea / eV	$\sigma_{ele}/25\,°C$
LLNO-Li 0	4.93×10^{-8}	0.371	1.97×10^{-10}
LLNO-Li 5	7.95×10^{-6}	0.354	2.81×10^{-10}
LLNO-Li 10	7.06×10^{-6}	0.355	3.04×10^{-9}
LLNO-Li 15	1.17×10^{-5}	0.355	3.25×10^{-9}
LLNO-Li 20	4.81×10^{-6}	0.354	4.07×10^{-9}
LLNO-Li 25	7.48×10^{-7}	0.346	6.81×10^{-8}

Fig. 4. Arrhenius diagram of ceramic pellets (color online)

The graph of Log σT in terms of 1000 / T is shown in Fig. 4. The fitted curves of all samples with different excess lithium contents are approximately linear. The activation energies of ceramic samples are listed in Table 1. LLNO-Li 0 has the highest activation energy of 0.371 eV. The activation energy decreased with the addition of excess lithium. The samples of LLNO-Li 5, LLNO-Li 10, LLNO-Li 15 and LLNO-Li 20 present similar activation energies of about 0.355 eV. LLNO-Li 20 exhibits the lowest activation energy of 0.346 eV. The activation

energies for all samples are close to the other traditional ceramic type Li-ion solid electrolytes.
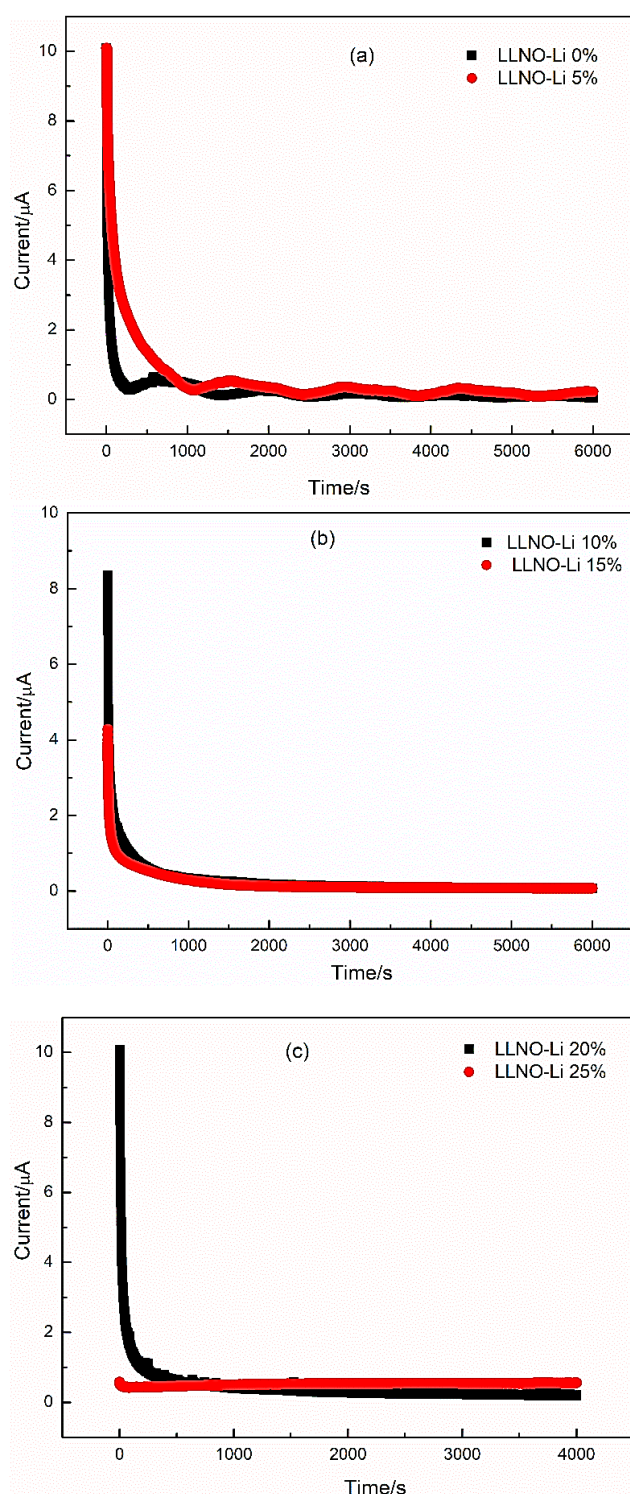

Fig. 5. DC polarization plots of ceramic pellets, (a) LLNO-Li 0, LLNO-Li 5, (b) LLNO-Li 10, LLNO-Li 15 and (c) LLNO-Li 20, LLNO-Li 25 (color online)

The electronic conductivity of the ceramic samples was determined by DC polarization test with ion-blocking Ag electrodes coated on both sides of the ceramic pellet. The result of the DC polarization test is shown in Fig. 5. For the samples of LLNO-Li 10, LLNO-Li 15, LLNO-Li 20 and LLNO-Li 25, after approximately 2000 s, the current reached a steady state, and the ionic current was completely blocked. For the samples of LLNO-Li 0 and LLNO-Li 5, the current fluctuates slightly during the DC polarization test but the overall is stable. The steady-state current was used to calculate the electronic conductivity of ceramic samples. For sample LLNO-Li 0 without excess lithium, both the ionic and electronic conductivity are extremely low. LLNO-Li 0 seems not equipped to conduct ions and electronics. The electronic conductivity of LLNO ceramic samples increases according to excess lithium contents, which is not a good phenomenon because high electronic conductivity may cause short circuit of devices, making it adverse to the application of solid electrolytes. The electronic conductivity of LLNO-Li 10, LLNO-Li 15 and LLNO-Li 20 samples is 3.04×10^{-9}, 3.25×10^{-9} and 4.07×10^{-9} S cm^{-1} at 25 °C, which is about three orders of magnitude lower than the corresponding total conductivity. So, LLNO-Li 10, LLNO-Li 15 and LLNO-Li 20 are pure Li-ion conductors. For sample LLNO-Li 25 with 25wt%-excess lithium, the ratio of electronic conductivity to total conductivity is 1%. So, LLNO-Li 25 cannot be regarded as a pure solid electrolyte due to its high electronic conductivity.

4. Conclusion

In the present study, LLNO ceramics with different excess lithium contents in raw materials was synthesized via a simple solid state reaction method. The structure and ionic conductivity of the ceramic samples were evaluated. The addition of 15-20 wt% lithium carbonate in raw materials can help LLNO obtain a good perovskite structure. Excess lithium can effectively balance the lithium volatilization loss in the process of high sintering temperature. Among all samples, the LLNO-Li 15 sample has the largest total conductivity of 1.17×10^{-5} S cm^{-1} at 25 °C, with the activation energy of 0.355 eV. The electronic conductivity of LLNO-Li 15 sample is 3.25×10^{-9} S cm^{-1} at 25 °C, which is about three orders of magnitude lower than its total conductivity. Further addition of excess lithium content leads to a decrease of conductivity for LLNO ceramic. The optimal excess lithium content is determined to be 15 wt%.

References

[1] J. Hao, Z. Wang, H. Gao, X. Li, B. Yang, X. He, J. Optoelectron. Adv. M. **25**(5-6), 221 (2023).

[2] Z. Yang, M. Nakayama, J. Phys. Soc. Jpn. **91**(9), 091010 (2022).

[3] X. Hu, S. Kobayashi, Y. H. Ikuhara, C. A. J. Fisher, Y. Fujiwara, K. Hoshikawa, H. Moriwake, K. Kohama, H. Iba, Y. Ikuhara, Acta Mater. **123**, 167 (2017).

[4] J.-Q. Zheng, Y.-F. Li, R. Yang, G. Li, X.-K. Ding, Ceram. Int. **43**(2), 1716 (2017).

[5] Y. Kawakami, M. Fukuda, H. Ikuta, M. Wakihara, Solid State Ion. **110**(3–4), 187 (1998).

[6] J. Hong, S. Kobayashi, A. Kuwabara, Y. H. Ikuhara, Y. Fujiwara, Y. Ikuhara, Molecules **26**(12), 3559 (2021).

[7] Z. Yang, R. E. Ward, N. Tanibata, H. Takeda, M. Nakayama, R. Kobayashi, Solid State Ion. **366–367**, 115662 (2021).

[8] Y. Maruyama, M. Nagao, S. Watauchi, I. Tanaka, J. Ceram. Soc. Jpn. **129**(8), 535 (2021).

[9] K. Kawahara, R. Ishikawa, K. Nakayama, T. Higashi, T. Kimura, Y. H. Ikuhara, N. Shibata, Y. Ikuhara, J. Power Sources **441**, 227187 (2019).

[10] O. M. Ozkendir, J. Optoelectron. Adv. M. **25**(5-6), 302 (2023).

[11] Z. Yang, S. Suzuki, N. Tanibata, H. Takeda, M. Nakayama, M. Karasuyama, I. Takeuchi, J. Phys. Chem. C **125**(1), 152 (2021).

[12] H. Li, X. Jiang, J. Zhang, J. Zhang, Mater. Today Commun. **34**, 105203 (2023).

[13] A. Itaya, K. Yamamoto, R. Inada, Y. Sakurai, Mater. Lett. **284**, 128941 (2021).

[14] X. Xiang, Z. Fang, X. Wang, Z. Zhao, H. Zhang, Y. Zhang, Int. J. Appl. Ceram. Technol. **20**(1), 14218 (2022).

_____
[*]Corresponding author: kongyazhou@hyit.edu.cn