*Supplementary information*

# The experimental identification of $Bi^{3+}$ dopants in $NaLuGeO_4$

## 1. Introduction

In order to provide some experimental proofs for the accurate identification of the $Bi^{3+}$ location sites in $NaLuGeO_4$, we have prepared two series of the samples and have measured the XRD, XPS, ICP and Raman properties of the samples in details. The experiments processes would be described in the first part and the results would be shown and discussed in the second part as follows.

## 2. Experimental

Firstly, the $Bi^{3+}$ dopants are expected to replace the $Na^+$ cations in the $NaLuGeO_4$, and thus we have prepared five typical samples on the basis of the stoichiometric ratio. The weights of raw materials and expected chemical formula are listed in Table S1.

Table S1. The weights of raw materials and chemical formula for $Bi^{3+}$ in $Na^+$ sites.

| No. | Chemical formula | $Na_2CO_3$ | $Lu_2O_3$ | $GeO_2$ | $Bi_2O_3$ |
|---|---|---|---|---|---|
| Na1% | $(Na_{0.99}Bi_{0.01})LuGeO_4$ | 0.1049 | 0.3979 | 0.2093 | 0.0047 |
| Na3% | $(Na_{0.97}Bi_{0.03})LuGeO_4$ | 0.1028 | 0.3979 | 0.2093 | 0.0140 |
| Na5% | $(Na_{0.95}Bi_{0.05})LuGeO_4$ | 0.1007 | 0.3979 | 0.2093 | 0.0233 |
| Na10% | $(Na_{0.95}Bi_{0.10})LuGeO_4$ | 0.0954 | 0.3979 | 0.2093 | 0.0466 |
| Na20% | $(Na_{0.80}Bi_{0.20})LuGeO_4$ | 0.0848 | 0.3979 | 0.2093 | 0.0932 |

Meanwhile, the $Bi^{3+}$ dopants are also expected to substitute the $Lu^{3+}$ sties in the $NaLuGeO_4$, and accordingly we have synthesized other five typical samples based on the stoichiometric ratio of raw materials as well. The weights of raw materials and the expected chemical formula are listed in the Table S2.

Table S2. The weights of raw materials and chemical formula for $Bi^{3+}$ in $Lu^{3+}$ sites.

| No. | Chemical formula | $Na_2CO_3$ | $Lu_2O_3$ | $GeO_2$ | $Bi_2O_3$ |
|---|---|---|---|---|---|
| Lu1% | $Na(Lu_{0.99}Bi_{0.01})GeO_4$ | 0.1060 | 0.3940 | 0.2093 | 0.0047 |
| Lu3% | $Na(Lu_{0.97}Bi_{0.03})GeO_4$ | 0.1060 | 0.3860 | 0.2093 | 0.0140 |
| Lu5% | $Na(Lu_{0.95}Bi_{0.05})GeO_4$ | 0.1060 | 0.3780 | 0.2093 | 0.0233 |
| Lu10% | $Na(Lu_{0.90}Bi_{0.10})GeO_4$ | 0.1060 | 0.3581 | 0.2093 | 0.0466 |
| Lu20% | $Na(Lu_{0.80}Bi_{0.20})GeO_4$ | 0.1060 | 0.3183 | 0.2093 | 0.0932 |

The raw materials were $Na_2CO_3$ (A.R.), $GeO_2$ (99.99%), $Lu_2O_3$ (99.99%), $Bi_2O_3$ (99.9%) and $Eu_2O_3$ (99.99%), which were weighed according to the stoichiometric ratio. The following experimental processes are same to the description in our paper, and thus we don’t repeat it here any more.

The Raman spectroscopy was measured by JY-HR800 micro-Raman with a 532 nm wavelength YAG laser with a laser spot diameter of 600 nm. The surface elemental analysis was performed using an X-ray photoelectron spectrometer (XPS, PHI-5702, Mg KR X-ray, 1253.6 eV). The ICP measurement was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES, IRIS ER/S, TJA Company). The phases and the crystal structures were characterized by the Rigaku D\Max-2400 X-ray diffractometer under Ni-filtered Cu Kα radiation.

## 2. Results and discussion

Figure S1 shows the XRD and standard card for the five samples $(Na_{1-x}Bi_x)LuGeO_4$ (a) and the other five samples $Na(Lu_{1-x}Bi_x)GeO_4$ (b). It can be seen that, even the $Bi^{3+}$ content has reached as high as 20mol%, the XRD peaks of all the samples did not change significantly, and the patterns can be well indexed into $NaLuGeO_4$. This is a surprising result and it indicates that the $Bi^{3+}$ dopants may be able to replace either $Na^+$ or $Lu^{3+}$ cations. Moreover, if the $Bi^{3+}$ ions have been surely incorporated into the expected sites, it means that the $Bi^{3+}$ locations in $NaLuGeO_4$ materials are possibly able to be controlled by the stoichiometric ratio of raw materials.

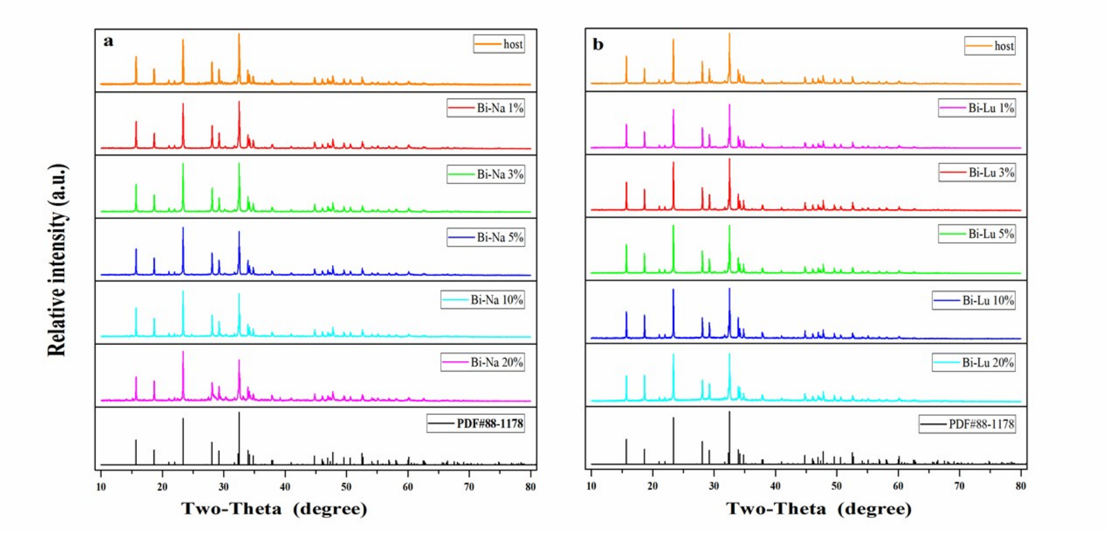

Figure S1. XRD patterns and standard cards for the five samples of $Bi^{3+}$ substituted at $Na^+$ sites (a) and the other five samples of $Bi^{3+}$ substituted at $Lu^{3+}$ sites (b)

In order to further confirm our above speculation, some typical samples have been subjected to the ICP measurements, and the result have been exhibited in Table S3. In order to reduce the influence of error, we choose the samples with larger $Bi^{3+}$ doping content (10%). It can be seen that the Na content of the $(Na_{0.95}Bi_{0.10})LuGeO_4$ sample (Na10%) is about 5.99%, and it has increased to 7.53% for the $Na(Lu_{0.90}Bi_{0.10})GeO_4$ sample (Lu10%). On the contrary, the Lu content (52.61wt%) of the Na10% is clearly higher than that (48.34wt%) of the Lu10% samples. It is reasonable that if the $Bi^{3+}$ ions replace the $Na^+$ cations, the Na content would be lower; but if the $Lu^{3+}$ sites are occupied by $Bi^{3+}$, the Lu content should be correspondingly decreased. This result indirectly suggest that the $Bi^{3+}$ dopants have entered the expected lattice sites of $Na^+$ or $Lu^{3+}$ because of the controlling by the stoichiometric ratio of raw materials.

Table S3. The ICP results of some typical samples (wt%)

| No. | Chemical formula | Na content | Lu content | Bi content |
|---|---|---|---|---|
| Na10% | $(Na_{0.95}Bi_{0.10})LuGeO_4$ | 5.99wt% | 52.61wt% | 5.12wt% |
| Lu10% | $Na(Lu_{0.90}Bi_{0.10})GeO_4$ | 7.53wt% | 48.34wt% | 5.37wt% |

In order to further confirm the results based on the ICP measurements, The surface elemental analysis of some typical samples was performed by XPS. In order to reduce the influence of error, we choose the samples with larger $Bi^{3+}$ doping content (10%) as well. Figure S2 shows the XPS spectra of three typical samples including the host, Na10% and Lu10%, respectively. At first, the XPS peak near 1070 eV belongs to Na 1s (a), while the two peaks at around 196 eV and 206 eV (b) can be attributed to Lu 4d5 and 4d3. Secondly, it can be clearly seen that the peak intensity of Na 1s in the Na10% sample is much lower than the intensity of the same peak in host (c), while the characteristic peaks of Lu element in the Lu10% sample also exhibit the same decreasing trend (d). Although the XPS is not very accurate for the quantitative analysis of elements, this decreasing trend still suggests that there are less Na content in the Na10% sample and also less Lu content in the Lu10% sample when compared with the host sample without $Bi^{3+}$ dopants. This result is consistent with the result of the ICP analysis and it also confirms that the $Bi^{3+}$ occupancy in $NaLuGeO_4$ materials can be well controlled by the stoichiometric ratio of raw materials.

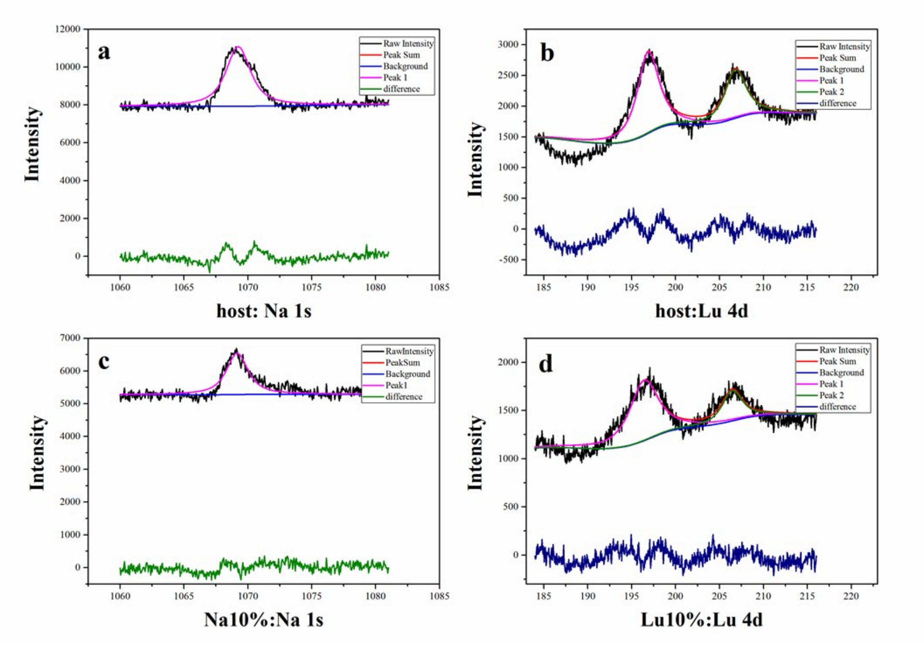

Figure S2. XPS results of three typical samples including the Na10% (a) Lu10% (b) and host (c,d), respectively.

Figure S3 shows the Raman spectra of the typical samples including Na1%, Na10%, Na20% (a) and Lu1%, Lu10%, Lu20% (b). It is found that the peaks in range 600-900 cm$^{-1}$ in the spectra can be attributed to the Ge-O bond stretching [1]. When Bi$^{3+}$ enters the Na$^{+}$ lattice, the Raman peaks decrease significantly as shown in Figure S3a. But, when Bi$^{3+}$ enters the Lu$^{3+}$ sites, the intensity of the Raman peaks in Figure S3b don't change significantly. Although the ionic radii of the Bi$^{3+}$ and Na$^{+}$ cations are similar, the substitution of Na$^{+}$ lattice by Bi$^{3+}$ will cause lattice distortion due to the significant differences between the valence states and electronegativity as exhibited in Table S4, corresponding to the variation of the Raman spectroscopy in Figure S3a. Therefore, the complete solubility will not occur for the substitutions of Na$^{+}$ by Bi$^{3+}$. However, substitution of Lu$^{3+}$ sites by Bi$^{3+}$ ions seems to be much milder and thus it has no significant effect on the lattice as shown in Figure S3b. At this stage, it is still difficult to answer which sites (Na$^{+}$ or Lu$^{3+}$) do the Bi$^{3+}$ ions prefer to occupy in NaLuGeO$_4$ materials, but we can say that both of the sites can be surely occupied by controlling the stoichiometric ratio of raw materials.

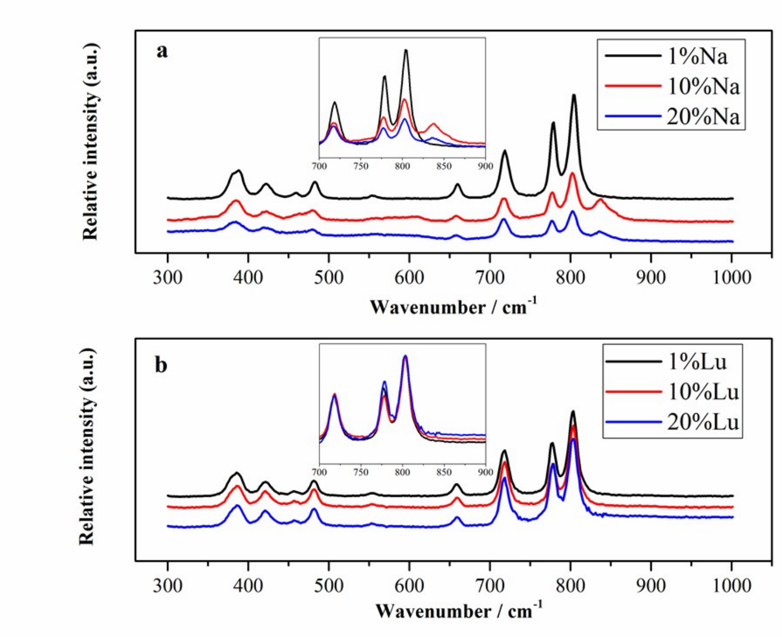

Figure S3. Raman spectra of the typical samples: Na1%, Na10%, Na20% (a) and Lu1%, Lu10%, Lu20% (b).

Moreover, Table S4 shows the comparison of the ion radius (six coordinations) and electronegativity of $Na^+$, $Lu^{3+}$, $Bi^{3+}$ ions. In the case of six coordinations, the ion radius of $Na^+$ (1.02 Å) is clearly closer to $Bi^{3+}$ (1.03 Å), but the electronegativity of $Lu^{3+}$ (1.399 eV) and $Bi^{3+}$ (1.431 eV) are closer.[2] According to the Hume-Rother rule [3], the ionic radius difference between $Bi^{3+}$ (1.03 Å) and $Lu^{3+}$ (0.86 Å) ions is 19.6%, which is higher than the threshold value 15% of good solubility pointed out in the Hume-Rothery rules. However, the valence states of $Bi^{3+}$ and $Lu^{3+}$ ions are the same. Accordingly, these above theoretical data will lead to the opposite conclusion and thus both the $Na^+$ and $Lu^{3+}$ sites may be occupied by the $Bi^{3+}$ dopants in theory.

Table S4. Ion radius (six coordinations) and electronegativity of $Na^+$, $Lu^{3+}$, $Bi^{3+}$ ions

| Ion | $r$ / Å | $r_{\text{difference}}$ / % | Electronegativity / eV |
|---|---|---|---|
| $Na^+$ | 1.02 | 0.98% | 1.024 |
| $Lu^{3+}$ | 0.86 | 19.76% | 1.431 |
| $Bi^{3+}$ | 1.03 | —— | 1.399 |

$r_{difference} = (r_{solute}-r_{solvent}) / r_{solvent} \times 100\%$

According to the above results, it can be concluded that the $Bi^{3+}$ occupancy can be well controlled by the stoichiometric ratio of raw materials. Although both the $Na^+$ and $Lu^{3+}$ cations can be replaced by the $Bi^{3+}$ dopants, in our article all the samples are synthesized according to the fixed chemical formula: $(Na_{1-x}Bi_x)LuGeO_4$. Therefore, in our work, it is very reasonable that the $Bi^{3+}$ ions should occupy the $Na^+$ sites in the $NaLuGeO_4$ materials.

## References

[1] B. Mihailova, D. Toncheva, M. Gospodinov, L. Konstantinov, Solid Stat. Commun. 1999, 112, 11-15.

[2] K. Li and D. Xue, J. Phys. Chem. A., 2006, 110, 11332-11337.

[3] https://en.wikipedia.org/wiki/Hume-Rothery_rules