

Supplementary information for

Ga-doped $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ mayenite oxide ion conductors: synthesis, defects, and electrical properties

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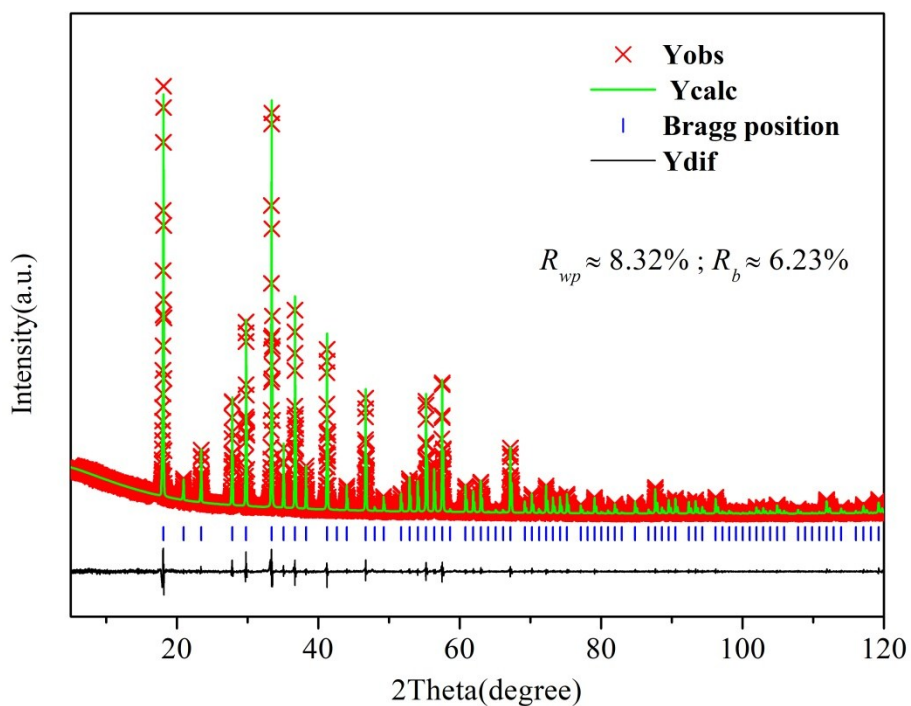


Figure S1. Rietveld fitting plot for the parent $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$.

Table S1. Final refined structural parameters of parent $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$. Lattice parameters: $a = 11.9947(6)$ Å, space group $\bar{I}43d$.

Atom	Site	x	y	z	Occupies	$B_{\text{iso}}(\text{Å}^2)$
Ca1	24d	0.1107(5)	0	1/4	0.862(3)	1.45(1)
Ca2	24d	0.041(1)	0	1/4	0.138(3)	3.0(2)
Al1	12a	3/8	0	1/4	1	0.37(8)
Al2	16c	-0.01811(9)	-0.01811(9)	-0.01811(9)	1	0.74(6)
O1	16c	0.0609(2)	0.0609(2)	0.0609(2)	1	1.6(1)
O2	48e	0.1033(2)	0.1949(2)	0.2874(2)	1	3.0(1)
O3	48e	0.267(9)	1.143(5)	1.00(1)	0.0416(1)	0.8(1)

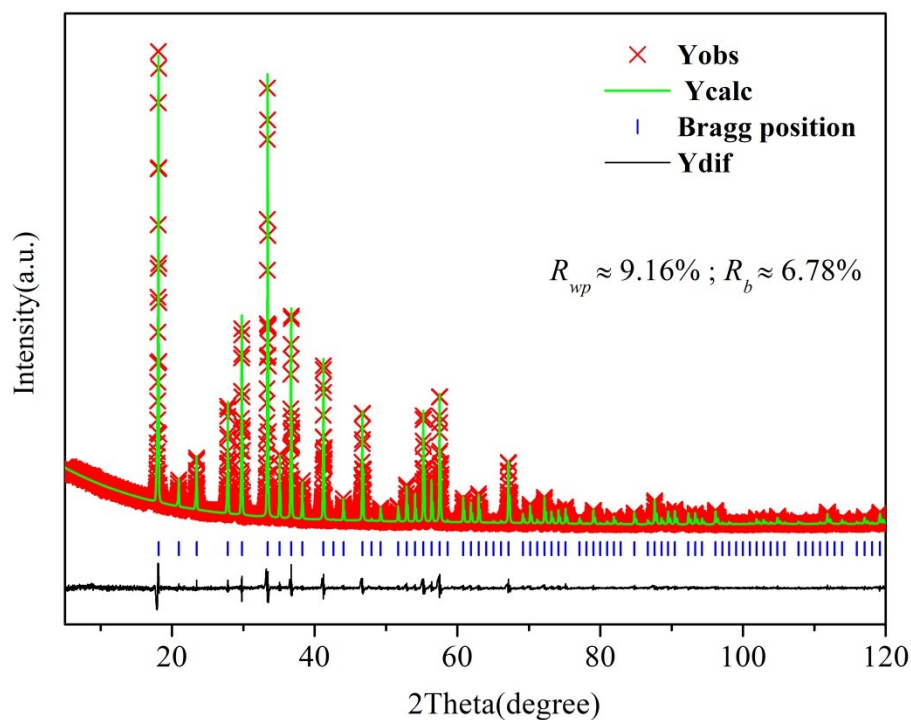


Figure S2. Rietveld fitting plot for the composition $\text{Ca}_{12}\text{Al}_{13.8}\text{Ga}_{0.2}\text{O}_{33+\delta}$.

Table S2. Final refined structural parameters of the composition $\text{Ca}_{12}\text{Al}_{13.8}\text{Ga}_{0.2}\text{O}_{33+\delta}$. Lattice parameters: $a = 11.9970(1)$ Å, space group $\overline{I}4\ 3d$.

Atom	Site	x	y	z	Occupies	$B_{\text{iso}}(\text{Å}^2)$
Ca1	24d	0.1063(1)	0	1/4	0.851(3)	0.66(5)
Ca2	24d	0.039(1)	0	1/4	0.149(3)	2.3(3)
Al1/Ga1	12a	3/8	0	1/4	0.982(1)/0.018(1)	2.2(1)
Al2/Ga2	16c	-0.0155(1)	-0.0155(1)	-0.0155(1)	0.986(3)/0.014(3)	2.47(8)
O1	16c	0.0613(3)	0.0613(3)	0.0613(3)	1	2.5(2)
O2	48e	0.1029(2)	0.1918(2)	0.2856(2)	1	1.34(9)
O3	48e	0.26(1)	0.164(5)	1.009(6)	0.0416(1)	1.03(2)

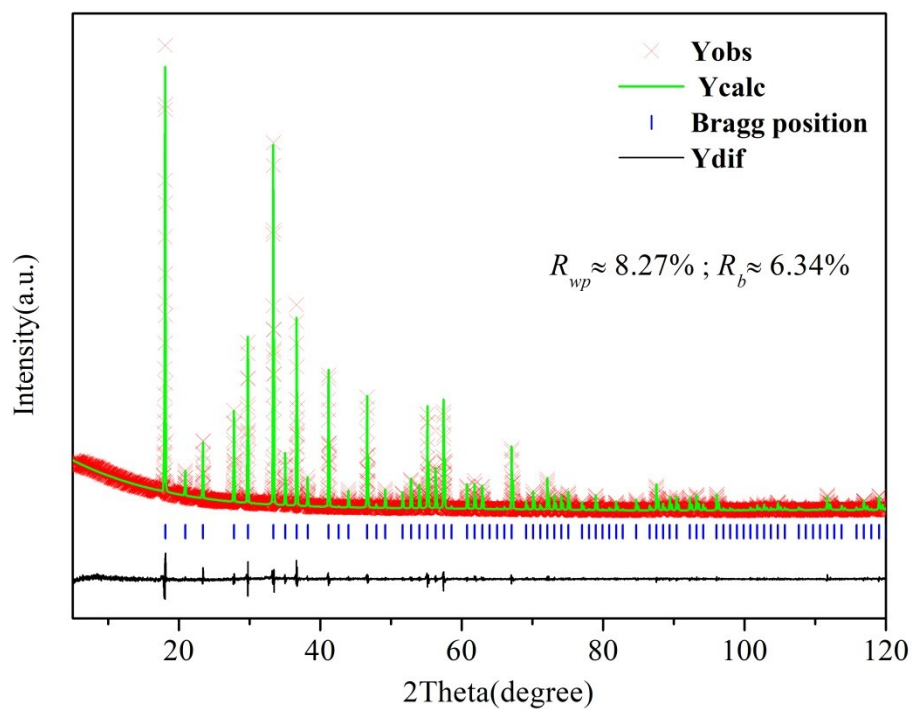


Figure S3. Rietveld fitting plot for the composition $\text{Ca}_{12}\text{Al}_{13.6}\text{Ga}_{0.4}\text{O}_{33+\delta}$.

Table S3. Final refined structural parameters of the composition $\text{Ca}_{12}\text{Al}_{13.6}\text{Ga}_{0.4}\text{O}_{33+\delta}$. Lattice parameters: $a = 11.9989(3)$ Å, space group $\overline{I}4\ 3d$.

Atom	Site	x	y	z	Occupies	$B_{\text{iso}}(\text{Å}^2)$
Ca1	24d	0.1062(4)	0	1/4	0.849(4)	0.66(7)
Ca2	24d	0.040(6)	0	1/4	0.151(4)	2.3(1)
Al1/Ga1	12a	3/8	0	1/4	0.966(1)/0.034(1)	2.2(1)
Al2/Ga2	16c	-0.0162(1)	-0.0162(1)	-0.0162(1)	0.974(2)/0.026(2)	2.4(1)
O1	16c	0.0578(3)	0.0578(3)	0.0578(3)	1	1.2(1)
O2	48e	0.1033(3)	0.1924(1)	0.2871(4)	1	0.56(3)
O3	48e	0.255(3)	0.161(8)	1.03(2)	0.0416(1)	2.53(2)

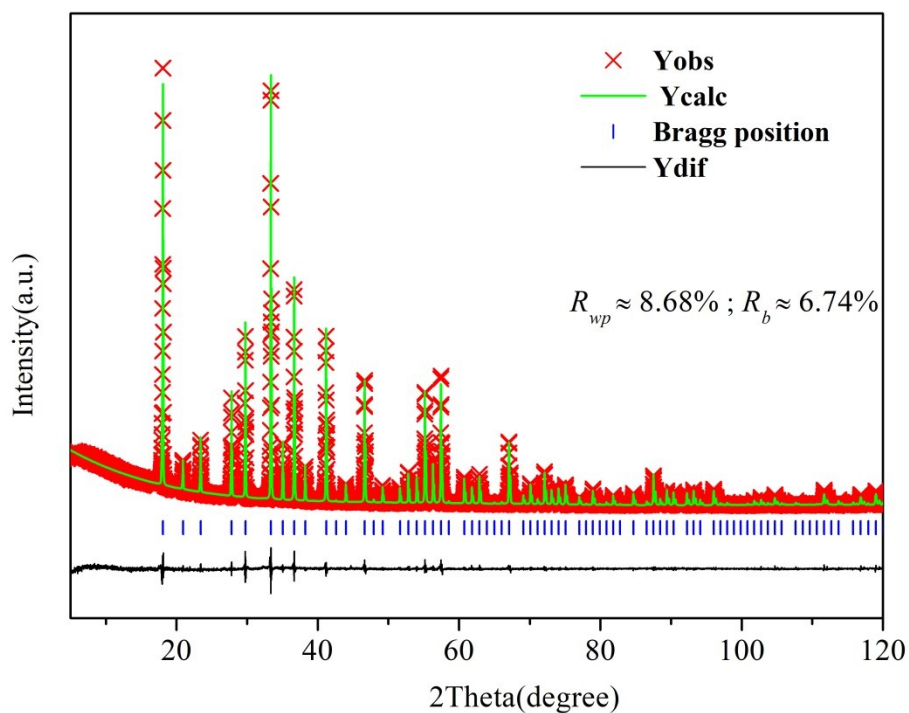


Figure S4. Rietveld fitting plot for the composition $\text{Ca}_{12}\text{Al}_{13.4}\text{Ga}_{0.6}\text{O}_{33+\delta}$.

Table S4. Final refined structural parameters of the composition $\text{Ca}_{12}\text{Al}_{13.4}\text{Ga}_{0.6}\text{O}_{33+\delta}$. Lattice parameters: $a = 12.0026(1)$ Å, space group $I\bar{4}3d$.

Atom	Site	x	y	z	Occupies	$B_{\text{iso}}(\text{Å}^2)$
Ca1	24d	0.1061(3)	0	1/4	0.847(1)	0.73(3)
Ca2	24d	0.044(8)	0	1/4	0.153(1)	2.3(2)
Al1/Ga1	12a	3/8	0	1/4	0.957(1)/0.043(1)	1.39(5)
Al2/Ga2	16c	-0.0164(1)	-0.0164(1)	-0.0164(1)	0.954(3)/0.046(3)	2.69(7)
O1	16c	0.0600(3)	0.0600(3)	0.0600(3)	1	0.9(1)
O2	48e	0.1014(2)	0.1882(3)	0.2847(2)	1	2.36(8)
O3	48e	0.2(1)	1.095(3)	0.99(7)	0.0416(1)	1.65(5)

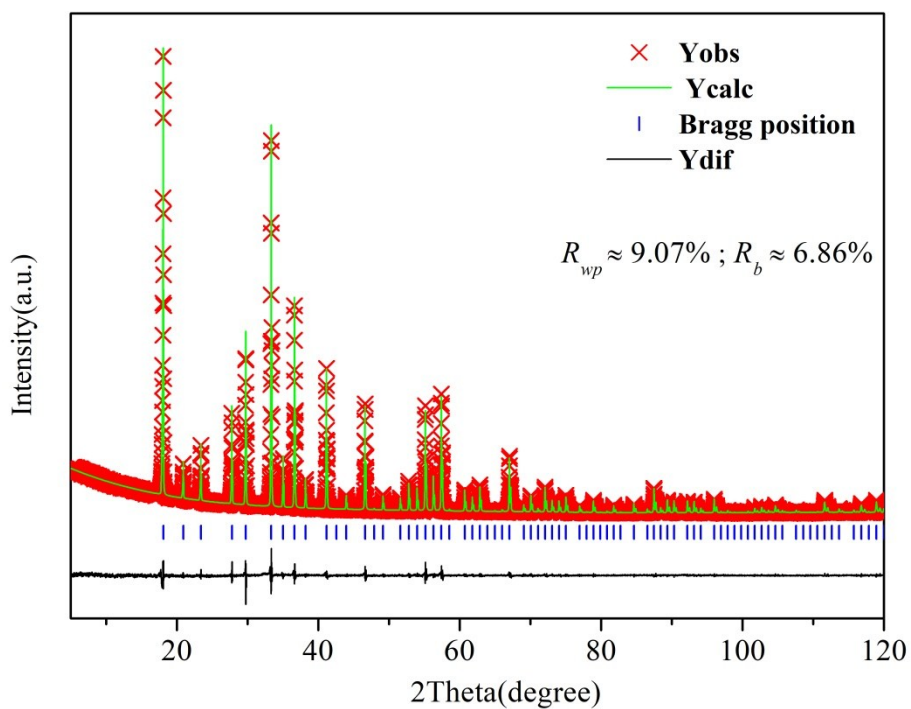


Figure S5. Rietveld fitting plot for the composition $\text{Ca}_{12}\text{Al}_{13.2}\text{Ga}_{0.8}\text{O}_{33+\delta}$.

Table S5. Final refined structural parameters of the composition $\text{Ca}_{12}\text{Al}_{13.2}\text{Ga}_{0.8}\text{O}_{33+\delta}$. Lattice parameters: $a = 12.0039(7)$ Å, space group $\overline{I}4\ 3d$.

Atom	Site	x	y	z	Occupies	$B_{\text{iso}}(\text{Å}^2)$
Ca1	24d	0.1081(6)	0	1/4	0.849(2)	0.34(5)
Ca2	24d	0.037(1)	0	1/4	0.151(2)	2.2(1)
Al1/Ga1	12a	3/8	0	1/4	0.945(1)/0.055(1)	1.4(1)
Al2/Ga2	16c	-0.0159(1)	-0.0159(1)	-0.0159(1)	0.944(1)/0.056(1)	2.3(1)
O1	16c	0.0595(3)	0.0595(3)	0.0595(3)	1	1.4(1)
O2	48e	0.1023(2)	0.1873(2)	0.2867(1)	1	2.89(7)
O3	48e	0.25(1)	1.125(4)	1.023(7)	0.0416(1)	1.21(1)

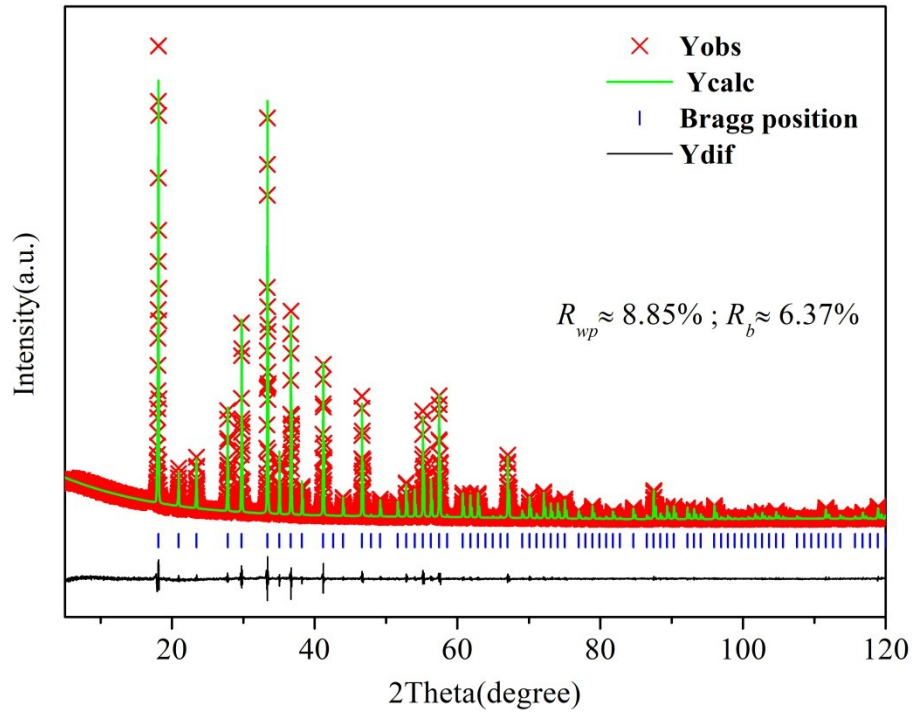


Figure S6. Rietveld fitting plot for the composition $\text{Ca}_{12}\text{Al}_{13.0}\text{Ga}_{1.0}\text{O}_{33+\delta}$.

Table S6. Final refined structural parameters of the composition $\text{Ca}_{12}\text{Al}_{13.0}\text{Ga}_{1.0}\text{O}_{33+\delta}$. Lattice parameters: $a = 12.0066(1)$ Å, space group $I\bar{4}3d$.

Atom	Site	x	y	z	Occupies	$B_{\text{iso}}(\text{Å}^2)$
Ca1	24d	0.1065(4)	0	1/4	0.837(1)	0.50(6)
Ca2	24d	0.034(1)	0	1/4	0.163(1)	0.92(7)
Al1/Ga1	12a	3/8	0	1/4	0.928(2)/0.072(2)	1.63(1)
Al2/Ga2	16c	-0.0167(1)	-0.0167(1)	-0.0167(1)	0.932(1)/0.068(1)	2.42(1)
O1	16c	0.0577(3)	0.0577(3)	0.0577(3)	1	2.6(2)
O2	48e	0.1027(2)	0.1888(2)	0.2859(2)	1	1.31(1)
O3	48e	0.245(9)	1.135(4)	0.99(1)	0.0416(1)	2.13(1)

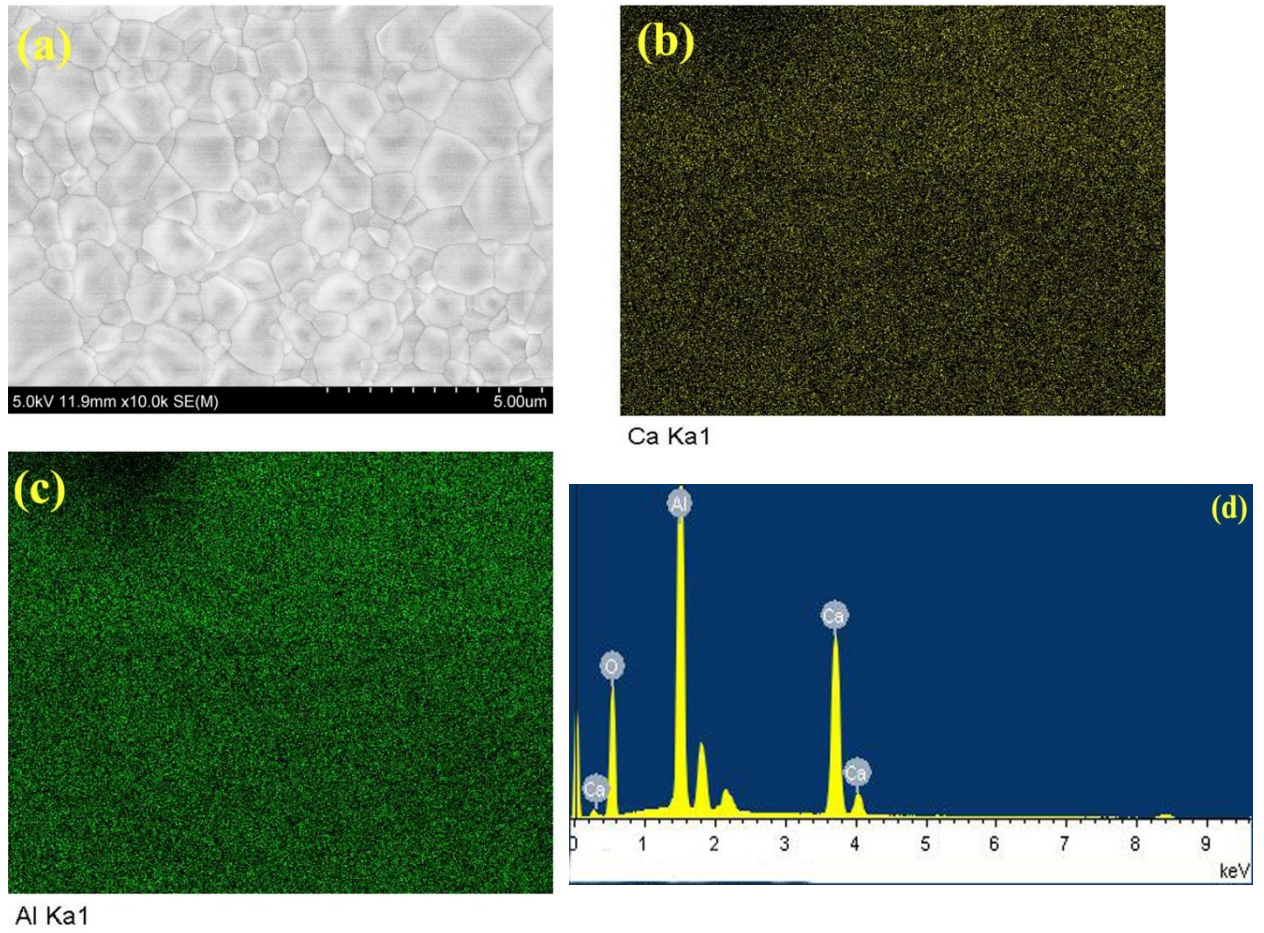


Figure S7. SEM micrograph of parent $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (a), and EDS element distribution maps of Ca (b), Al (c); picture (d) shows the element concentrations, the un-labeled peak is ascribed to the Au element that sprayed on the surface of the ceramic pellet before measurements. The relative element ratio for Ca : Al was revealed to be 12 : 14.3.

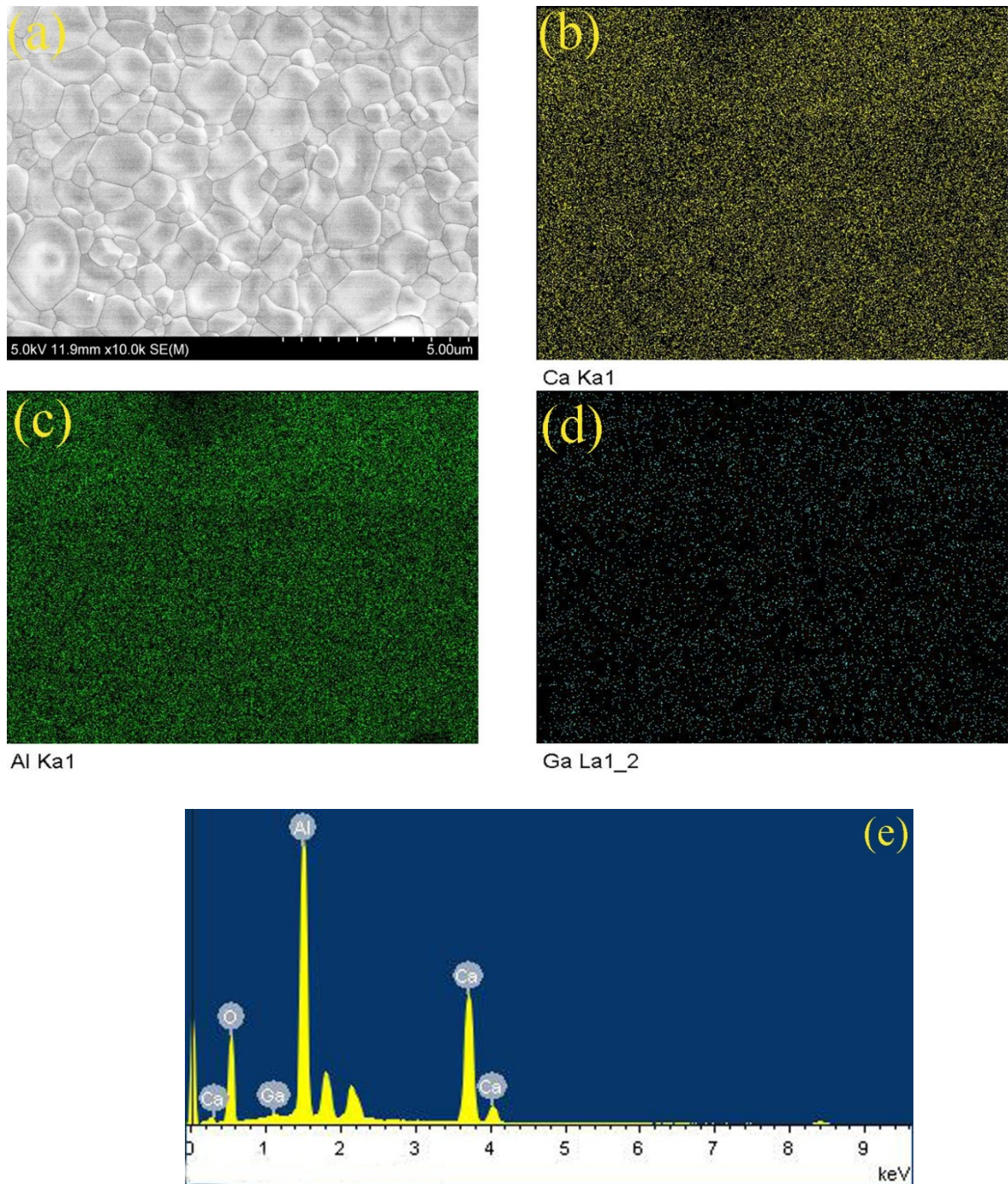


Figure S8. SEM micrograph of the composition $\text{Ca}_{12}\text{Al}_{13.8}\text{Ga}_{0.2}\text{O}_{33}$ (a), and EDS element distribution maps of Ca (b), Al (c), and Ga (d) ; picture (e) shows the element concentrations, the un-labeled peak is ascribed to the Au element that sprayed on the surface of the ceramic pellet before measurements. The relative element ratios for Ca : Al : Ga were revealed to be 12 : 13.74 : 0.23 .

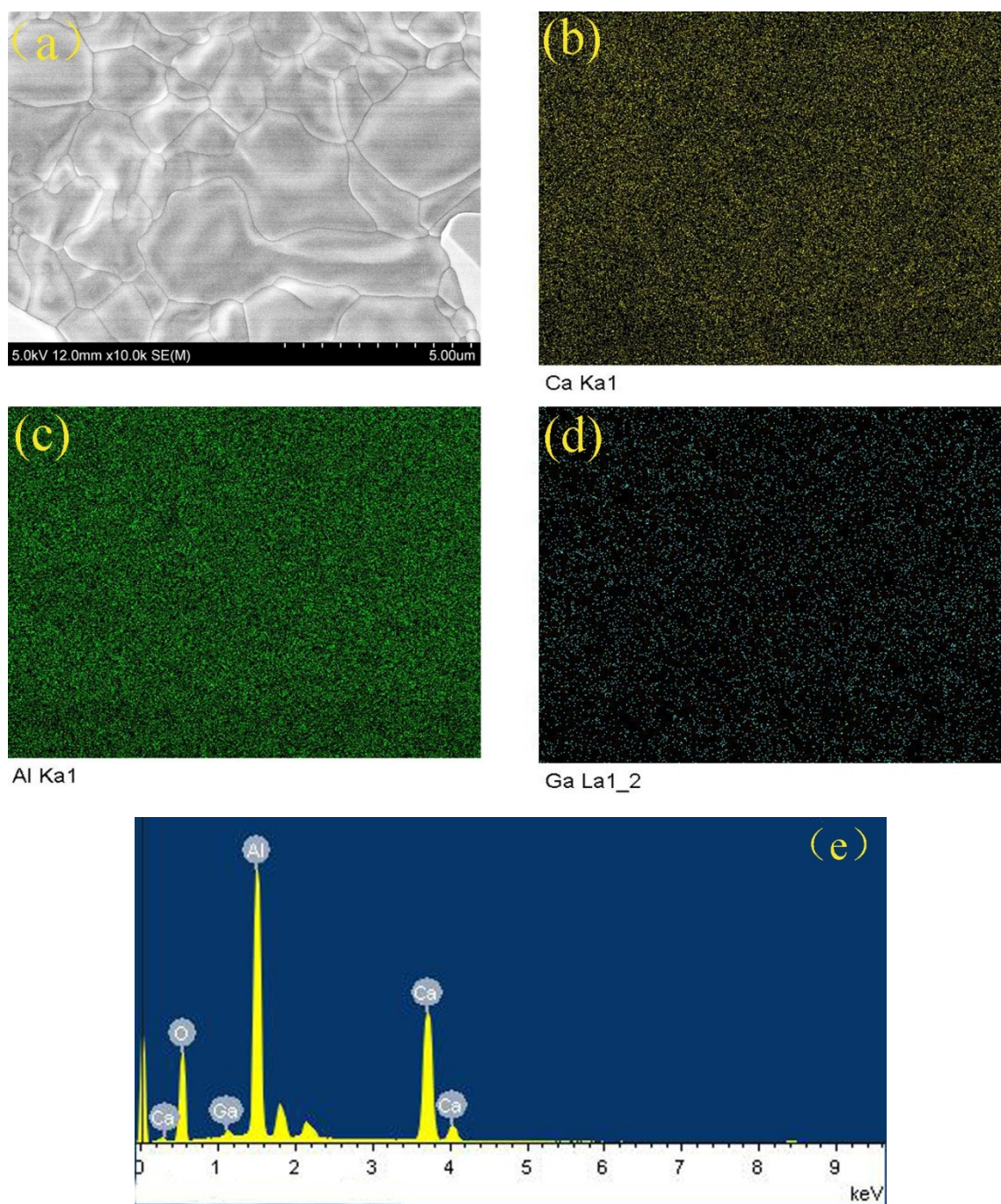


Figure S9. SEM micrograph of the composition $\text{Ca}_{12}\text{Al}_{13.6}\text{Ga}_{0.4}\text{O}_{33}$ (a), and EDS element distribution maps of Ca (b), Al (c), and Ga (d) ; picture (e) shows the element concentrations, the un-labeled peak is ascribed to the Au element that sprayed on the surface of the ceramic pellet before measurements. The relative element ratios for Ca : Al : Ga were revealed to be 12 : 13.65 : 0.36

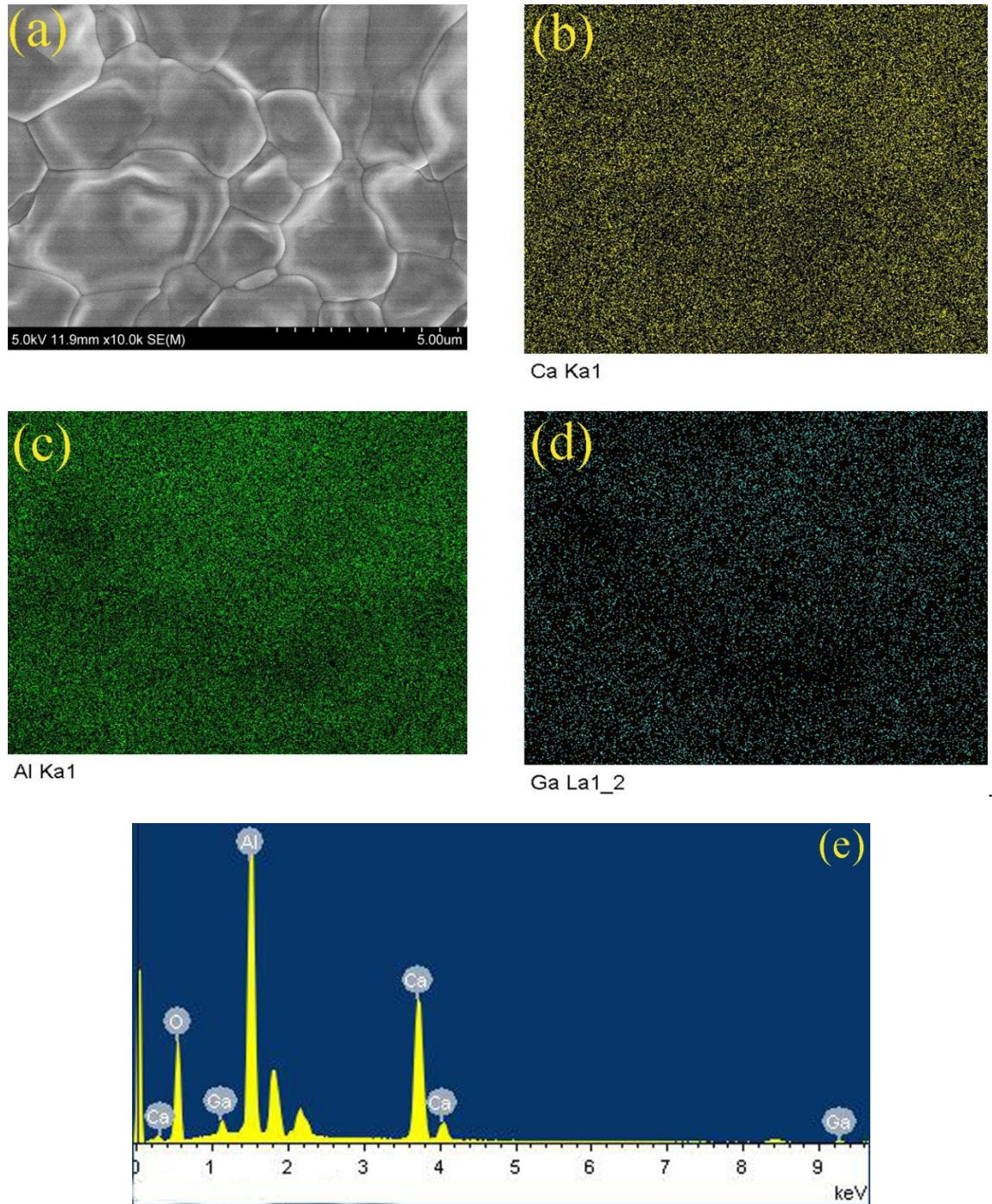


Figure S10. SEM micrograph of the composition $\text{Ca}_{12}\text{Al}_{13.4}\text{Ga}_{0.6}\text{O}_{33}$ (a), and EDS element distribution maps of Ca (b), Al (c), and Ga (d) ; picture (e) shows the element concentrations, the un-labeled peak is ascribed to the Au element that sprayed on the surface of the ceramic pellet before measurements. The relative element ratios for Ca : Al : Ga were revealed to be 12 : 13.37 : 0.62

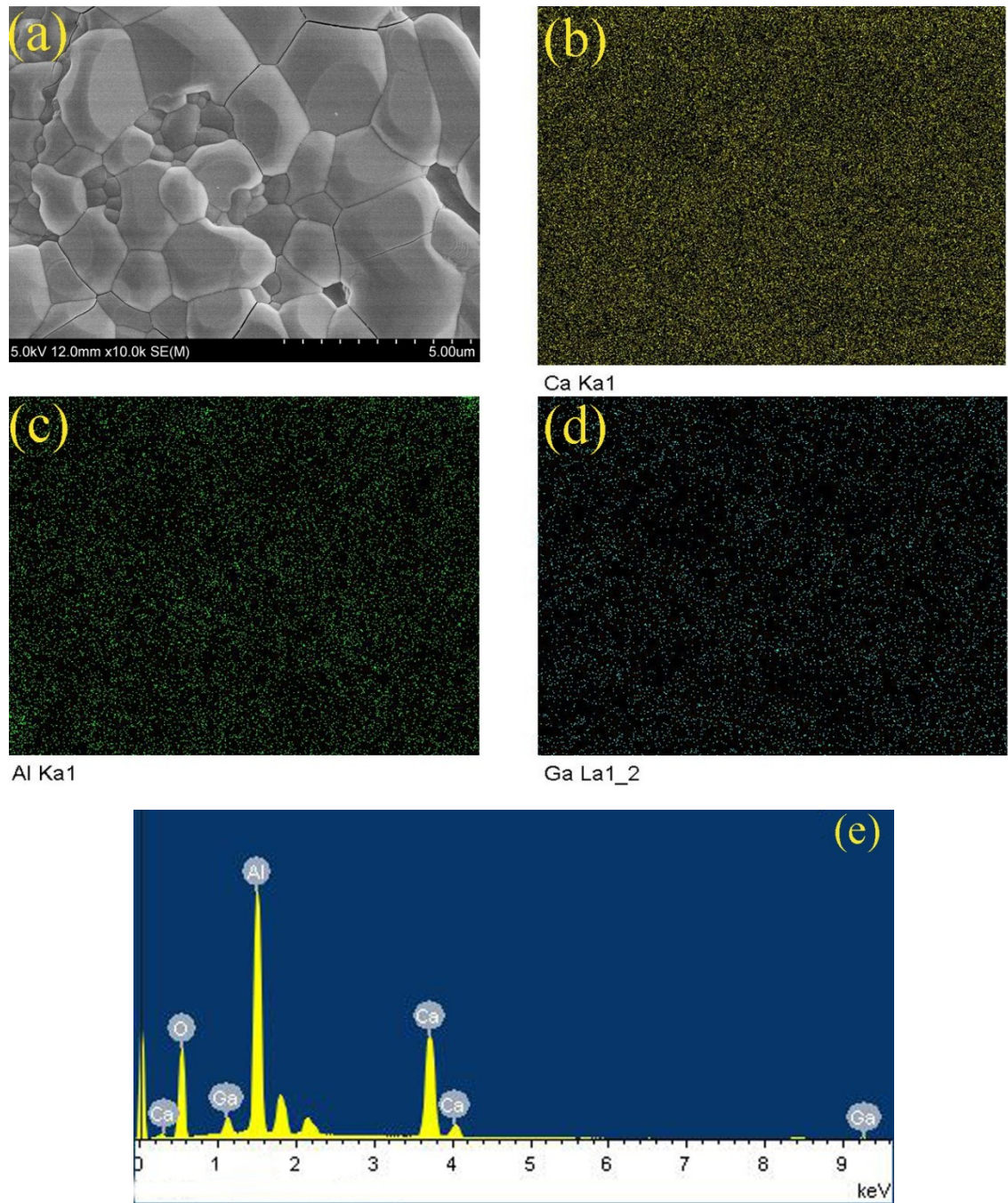


Figure S11. SEM micrograph of the composition $\text{Ca}_{12}\text{Al}_{13.2}\text{Ga}_{0.8}\text{O}_{33}$ (a), and EDS element distribution maps of Ca (b), Al (c), and Ga (d) ; picture (e) shows the element concentrations, the un-labeled peak is ascribed to the Au element that sprayed on the surface of the ceramic pellet before measurements. The relative element ratios for Ca : Al : Ga were revealed to be 12 : 13.14 : 0.81

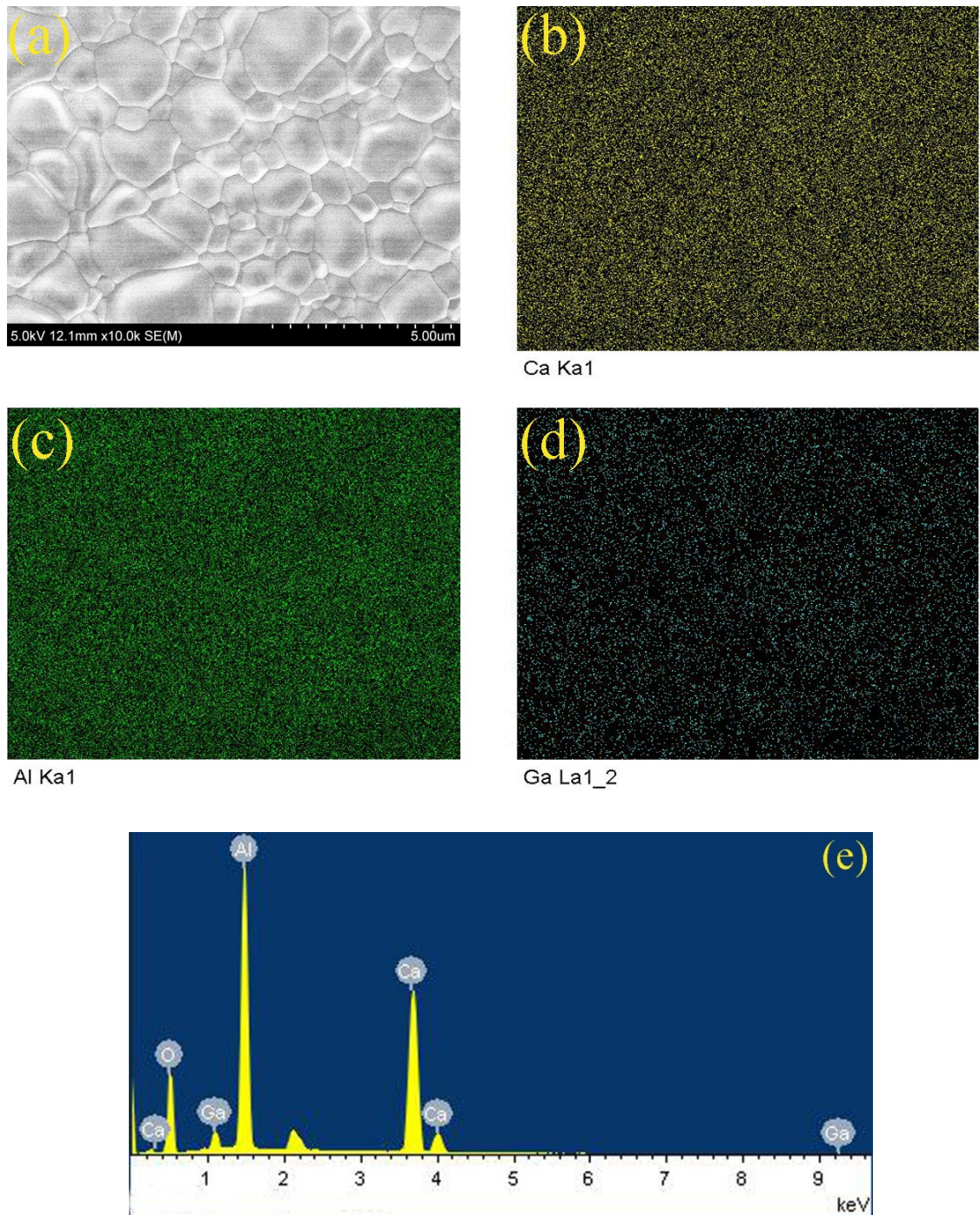


Figure S12. SEM micrograph of the composition $\text{Ca}_{12}\text{Al}_{13.0}\text{Ga}_{1.0}\text{O}_{33}$ (a), and EDS element distribution maps of Ca (b), Al (c), and Ga (d) ; picture (e) shows the element concentrations, the un-labeled peak is ascribed to the Au element that sprayed on the surface of the ceramic pellet before measurements. The relative element ratios for Ca : Al : Ga were revealed to be 12 : 13.11 : 0.92

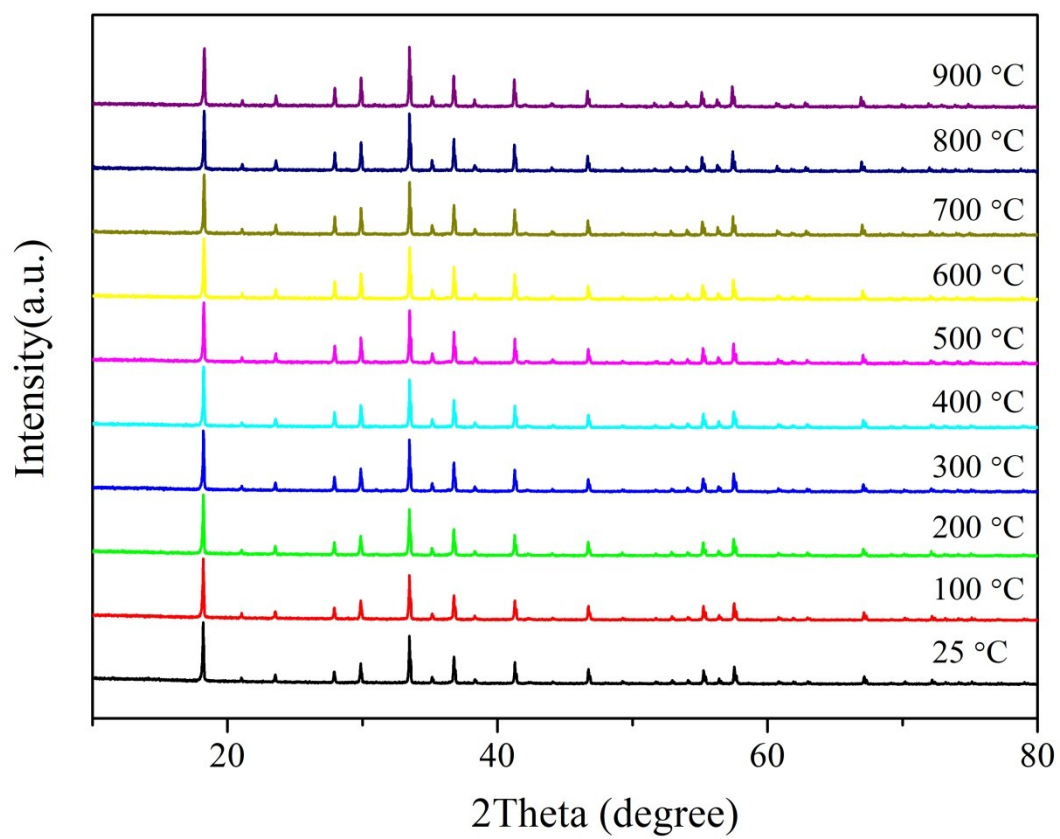


Figure S13. In-situ VT-XRD patterns of the sample $x = 0.4$