Rare Earth Ion-Doped $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$ (R = Yb, Y, Dy, Eu, Sm) Garnet-Type Microwave Ceramics for 5G Application

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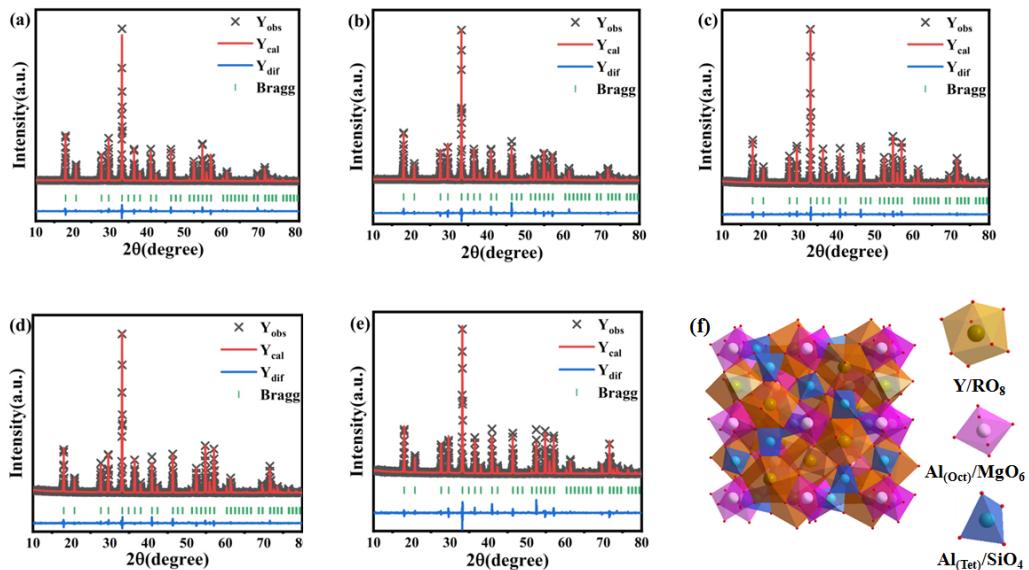
Figure S1. Rietveld refinement results of $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$(R=Yb, Y, Dy, Eu, Sm) ceramics (a) R=Yb; (b) R=Y; (c) R=Dy; (d)R=Eu;(e) R=Sm; (f) The crystal structure pattern of $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$ ceramic.
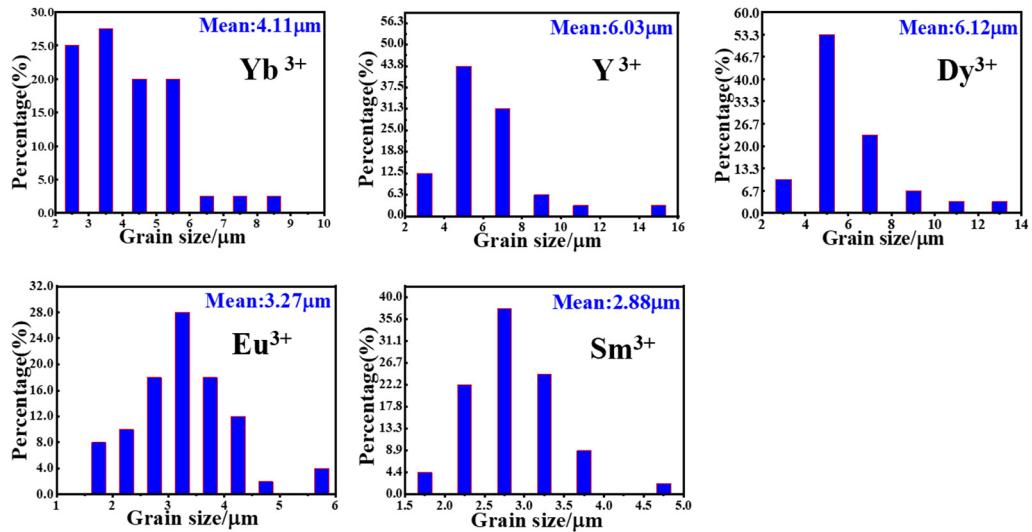
Figure S2. The grain size distribution of each sample.

Table S1 The bond ionicity f_i (%) of $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$ ceramics.

R	Yb	Y	Dy	Eu	Sm
Y-O	94.987	94.900	94.921	94.881	94.847
Al$_{(Oct)}$-O	80.648	80.747	80.638	80.749	80.897
Al$_{(Tet)}$-O	85.482	85.476	85.488	85.522	85.421
$\triangle f_i$	87.039	87.041	87.015	87.051	87.055

Table S2 The lattice energy U (kJ/mol) of $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$ ceramics.

R	Yb	Y	Dy	Eu	Sm
Y-O	22263.5586	22106.1459	22162.1090	22130.0663	22053.9339
Al$_{(Oct)}$-O	21909.7255	22003.6402	21895.3806	21995.7769	22143.7854
Al$_{(Tet)}$-O	33500.5304	33595.9648	33863.8348	33470.0917	33333.8267

U_{avg}	25891.2715	25901.9170	25973.7748	25865.3117	25843.8487

Table S3 The bond energy E (kJ/mol) of $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$ ceramics.

R	Yb	Y	Dy	Eu	Sm
Y-O	220.2495	218.7317	218.4487	218.0332	216.9003
$Al_{(Oct)}$-O	222.3202	225.4366	222.0543	223.9295	226.7216
$Al_{(Tet)}$ -O	307.7420	309.4896	307.7952	307.1756	304.1840
E_{avg}	250.1039	251.2193	249.433	249.713	249.269

Table S4 The bond valence V_{ij} of $Y_{2.95}R_{0.05}MgAl_3SiO_{12}$ ceramics.

R	Yb	Y	Dy	Eu	Sm
V_{Y-O}	3.0533	2.8207	2.9056	2.8640	2.7547
$V_{Al(Oct)-O}$	2.4473	2.5534	2.4315	2.5445	2.7187
$V_{Al(Tet)-O}$	3.1067	3.1901	3.1093	3.0801	2.9649

Table S5 The Phonon parameters obtained from the fitting of the infrared reflectivity

spectra of $Y_{2.95}Dy_{0.05}MgAl_3SiO_{12}$ ceramic.

Mode	ω_{oj}	ω_{pj}	γ_j	$\triangle\varepsilon_j$	$\tan\delta_j\times10^{-4}$
1	163.94	85.064	22.91	0.269	0.14
2	217.66	93.144	20.153	0.183	0.0926
3	341.12	154.74	89.178	0.206	0.261

4	469.59	371.7	52.665	0.627	0.112
5	519.76	295.01	30.185	0.322	0.0581
6	577.94	118.4	13.299	0.042	0.023
7	694.27	385.45	50.353	0.308	0.0725
8	773.86	427.4	99.71	0.305	0.129
9	882.52	250.54	60.823	0.0806	0.0689
10	950.39	235.07	43.703	0.0612	0.046
$Y_{2.95}Dy_{0.05}MgAl_3SiO_{12}$		$\varepsilon_{cal}=8.55$		$\tan\delta_{cal}=1.21\times10^{-4}$

Details of P-V-L-calculation on $Y_3Al_5O_{12}$ garnet-type ceramics

Phillips et al.[1,2] defined the relationship between crystal parameters and chemical bond properties for A_NB_{8-N} type binary crystals. Levine[3] perfected the above theory and solved the problem of chemical bond calculation in A_mB_n type binary crystals. Zhang et al.[4] developed a method to decompose complex polycrystals into crystal binary bonds when the crystal structure, coordination environment, and the ratio of elements in the crystal molecular formula were determined. The complex crystals $Y_3Al_5O_{12}$ can be decmposed into the sum of following binary crystals:

$$Y_3Al_5O_{12}=3(YO_2)+2(Al_{(Oct)}O_{3/2})+3(Al_{(Tet)}O) \tag{1}$$
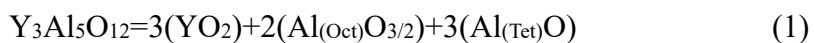
1. The formula of the bond ionicity:

The bond ionicity (f_i) of each chemical bond can be calculated by the equation(2):

$$f_i = \frac{(C^u)^2}{(E_g^u)^2} \qquad (2)$$

where E_g^u is the average energy gap for the type bond, C^u is the heteropolar part of E_g^u. C^u and E_g^u can be calculated as following:

$$\left(E_g^u\right)^2 = (E_h^u)^2 + (C^u)^2 \qquad (3)$$

$$E_h^u = \frac{39.74}{(d^u)^{2.48}} \qquad (4)$$

$$C^u = 14.4 \cdot b^u \cdot exp(-k_s^u d^u/2)[(Z_A^u)^* - n(Z_B^u)^*/m] \cdot (d^u/2)^{-1} \qquad (5)$$

where $(Z_A^u)^*$ and $(Z_B^u)^*$ are the effective number of valence electrons on cation A and effective number of valence electrons on anion B, respectively. b is a correction factor, $exp(-k_s^u d^u/2)$ is the Thomas-Fermi screening factor, it can obtained by the following equations:

$$k_s = \left(\frac{4k_F^u}{\pi \alpha_B}\right)^{1/2} \qquad (6)$$

$$k_F^u = [3\pi^2(N_e^u)]^{1/3} \qquad (7)$$

$$N_e^u = n_e \cdot \frac{\Sigma_u d^{u3} N_b^u}{d^3} \qquad (8)$$

$$n_e = \frac{(Z_A^u)^*}{N_{CA}} + \frac{(Z_B^u)^*}{N_{CB}} \qquad (9)$$

where α_B is the Bohr radius, n_e the number of effective valence electrons per u bond, N_b^u is the number of bonds per cubic centimeter.

2. The formula of the bond lattice energy:

For any chemical bond u, its lattice energy U_b^u can be calculated according to the P-V-L theory:

$$U_b^u = U_{bc}^u + U_{bi}^u \qquad (10)$$

$$U_{bc}^u = 2100m\frac{(Z_+^u)^{1.64}}{(d^u)^{0.75}} \cdot f_c^u \tag{11}$$

$$U_{bi}^u = 1270\frac{(m+n)Z_+^u \cdot Z_-^u}{(d^u)^{0.75}} \cdot \left(1 - \frac{0.4}{d^u}\right) \cdot f_i^u \tag{12}$$

where U_{bc}^u and U_{bi}^u are the U contributed by the ionic part and the covalent part of

the binary crystal, respectively. Z_+^u and Z_-^u are the valence of the cation and the

valence of the anion in the u bond.

3. The formula of the bond energy:

The bond energy (E) can be obtained by the following equations:

$$E^u = t_c E_c^u + t_i E_i^u \tag{13}$$

$$E_i^u = \frac{33200}{d^u} \tag{14}$$

$$E_c^u = \frac{(r_{CA}+r_{CB})}{d^u} \times (E_{A-A} \times E_{B-B})^{\frac{1}{2}} \tag{15}$$

$$t_i + t_c = 1 \tag{16}$$

$$t_i = \left|\frac{(S_A - S_B)}{6}\right| \tag{17}$$

where r_{CA} and r_{CB} are the covalent radii; E_{A-A} and E_{B-B} are the homonuclear bond

energy, which can be obtained from the handbook of bond energies. t_i and t_c are

ionic and covalent proportional coefficient of an individual bond u. S_A and S_B are

the electronegativities of A and B ions.

Reference:

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