Enabling highly efficient and broadband electromagnetic wave absorption by tuning impedance match in high-entropy transition metal diborides (HE TMB₂)

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Abstract: The advance in communication technology has triggered worldwide concern on electromagnetic wave pollution. To cope with this challenge, exploring high-performance electromagnetic (EM) wave absorbing materials with dielectric and magnetic losses coupling is urgently required. Of the EM wave absorbers, transition metal diborides (TMB₂) possess excellent dielectric loss capability. However, akin to other single dielectric materials, poor impedance match leads to inferior performance. High-entropy engineering is expected to be effective in tailoring the balance between dielectric and magnetic losses through compositional design. Herein, three HE TMB₂ powders with nominal equimolar TM including HE TMB₂-1 (TM = Zr, Hf, Nb, Ta), HE TMB₂-2 (TM = Ti, Zr, Hf, Nb, Ta), and HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta) have been designed and prepared by one-step boro/carbothermal reduction. As a result of synergistic effects of strong attenuation capability and impedance match, HE TMB₂-1 shows much improved performance with the optimal minimum reflection loss (RL_{min}) of −59.6 dB (8.48 GHz, 2.68 mm) and effective absorption bandwidth (EAB) of 7.6 GHz (2.3 mm). Most impressively, incorporating Cr in HE TMB₂-3 greatly improves the impedance match over 1–18 GHz, thus achieving the RL_{min} of −56.2 dB (8.48 GHz, 2.63 mm) and the EAB of 11.0 GHz (2.2 mm), which is superior to most other EM wave absorbing materials. This work reveals that constructing high-entropy compounds, especially by incorporating magnetic elements, is effectual in tailoring the impedance match for highly conductive compounds, i.e., tuning electrical conductivity and boosting magnetic loss to realize highly efficient and broadband EM wave absorption with dielectric and magnetic coupling in

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single-phase materials.

Keywords: transition metal diboride (TMB₂); high-entropy (HE) ceramics; electronic structure; microwave absorption; dielectric and magnetic losses coupling

1 Introduction

The ubiquitous electromagnetic (EM) wave pollutions accompanying the massive usage of wireless communication technologies have evolved into worldwide threats, which have harmful impacts on not only biological health but also normal operation of electronic devices [1–3]. To tackle this hazard, EM wave absorbing materials that are capable of converting EM energy into thermal energy or other forms of energy have drawn considerable attentions [4,5]. Thus, significant efforts have been made on exploring EM wave absorbing materials with thin thickness, light weight, high efficiency, and broadband absorption over decades.

In essence, the absorption of EM energy is implemented by the interactions between electric and/or magnetic dipoles of materials and EM waves. Since EM waves are made up of oscillating electric and magnetic fields, the attenuation of one of them will lead to a corresponding change of the other, which in turn results in the dissipations of the entire EM waves [4]. To date, a bunch of EM wave absorbing materials based on dielectric loss or magnetic loss mechanism have been developed. For instance, dielectric loss-type absorbers include carbon fiber (CF) [6], carbon nanotube (CNT) [7], reduced graphene oxide (rGO) [8], conductive polymer [9], oxides (silicon oxide [10], zinc oxide [11], etc.), transition metal sulfides [12], silicon carbide [13], and 2D transition metal carbides/nitrides/carbonitrides (MXenes) [14], and magnetic loss-type absorbers consist of ferrites [15–17] and magnetic metals [18–20]. Although dielectric loss-type EM absorbing materials exhibit high attenuation constant (α) mainly derived from dielectric loss, they are still hindered by limited absorption capacity and narrow effective absorption bandwidth (EAB) due to the mismatch between the complex permittivity and the complex permeability. In specific, highly conductive materials tend to form conductive framework at the surface and result in skin effects, which prevent the EM waves from penetrating into materials and reduce the occurrence of multi-attenuations [6,7]. As for

magnetic loss-type absorbers, they take advantages of a proper magnetization value and a relatively high Curie temperature but also suffer from a sudden decrease of permeability in high frequency due to the Snoek's limit [16,21,22]. Hence, various efforts have been carried out to realize dielectric and magnetic losses coupling and impedance matching, which can be achieved through composite construction [6,16,23–25], elemental doping [10], and structural design [26,27]. Although impedance match can be effectively achieved by the foregoing methods, complex experimental procedures and difficulties in accurately controlling nanostructures and interfaces are still unignorable issues. In addition, for applications in high-temperature environments, problems including poor thermal stability, oxidation susceptibility, and inferior corrosion resistance also need to be solved. It is thus significant to realize dielectric and magnetic losses coupling in single-phase materials that possess highly efficient EM wave absorption performance, easy processability, good thermal stability, and good resistance to oxidation and corrosion.

As the main member of the ultrahigh temperature ceramic (UHTC) family, transition metal diborides (TMB₂) crystallize in a AlB₂-type hexagonal structure with metallic bonding between TM atoms, ionic-covalent bonding between TM and B atoms, and covalent bonding between B atoms, which endow them high melting temperature, good thermal and chemical stabilities, good oxidation and corrosion resistance, as well as high electrical and thermal conductivities [28–31]. Intriguingly, in the crystal structure of TMB₂, there exhibit alternately graphite-like boron layers and transition metal layers, whose metallic features derived mainly from TM *d* states and partly from B 2*p_z* states [30–32]. Generally, the interaction between the incident electric field and electric dipoles leading to the dissipation of electromagnetic energy is referred as the dielectric loss ability, which counts on conductivity loss and relaxation polarizations in GHz range [33]. The electron migration due to the natural electrical conductivity of TMB₂ will lead to the reduction of electromagnetic energy in the form of conduction loss.

In this light, TMB_2 with good thermal stability, oxidation and corrosion resistance, and good dielectric loss capability are promising as EM wave absorbing materials. However, akin to the foregoing dielectric loss-type absorbers, the conductivity of TMB_2 is too high that a continuous conduction current is formed at the surface, which leads to poor impedance match and inferior EM wave absorption performance [6,7]. As demonstrated by Jian *et al.* [34], the reflection loss (RL) values of pure ZrB_2 are larger than -5 dB within the thickness of 1–5 mm in the frequency range of 2–18 GHz. Therefore, it is necessary to tailor the balance between dielectric loss and magnetic loss in TMB_2 for achieving efficient and broadband EM wave absorption capability.

In the light of localized states of TM d and B p electrons in TMB_2 , the electrical conductivity can be tuned by controlling the disorder in a fixed system size, i.e., with the same carrier density, the increasing of the degree of randomness in a fixed lattice can lead to the reduction of conductivity due to enhanced electron and phonon scattering [30,31,35–37]. Inspiringly, incorporating multiple principle elemental species into a single lattice with random occupancy is an effective way to increase the entropy and swell the randomness in the lattice [38–40]. In specific, according to Boltzmann's equation about the relationship of the configurational entropy per mole (ΔS_{conf}) and the complexation of a system ($\Delta S_{\text{conf}} = R \ln n$), the entropy increases with the number of elements (n) and reaches its maximum when all the species possess the same fraction [38,39]. Thus, it is an effective and efficient way to tune the electrical conductivity by developing high-entropy transition metal diboride (HE TMB_2).

In addition to tuning the electrical conductivity, enhancing magnetic loss ability through compositional design is also a key approach to realize impedance matching. Due to the paramagnetic features of TMB_2 (TM = Ti, Zr, Hf, Nb, Ta, etc.), their magnetic loss capabilities are often overlooked [34,41,42]. However, the magnetic loss capabilities of TMB_2 at GHz range are worthy of noting based on the following reasons. Firstly, due to the absence of unpaired electrons, most TMB_2 (TM = Ti, Zr, Hf, Nb, Ta, etc.) exhibit no magnetic ordering without external magnetic field but show anisotropy of magnetic susceptibility along and perpendicular to the six-fold c -axis of the hexagonal structure encountering alternating EM wave magnetic

field, which might lead to resonance loss correlating to the anisotropy field [27]. Secondly, experimental works have found that CrB_2 exhibits chromium-like antiferromagnetic helical magnetic structure [43,44], which is expected to possess high permeability. Especially when HE TMB_2 is formed with severe lattice distortion, an extra energy consumption is expected for the realignment of antiparallel spin moments. Therefore, incorporating CrB_2 into HE TMB_2 contributes to the decreased permittivity but increased permeability, which will further result in the improved impedance match as well as strong and broadband absorption performance. Thirdly, a host of defects are introduced by high configurational entropy construction in HE TMB_2 , which exhibit spin paramagnetism to some extent due to the presence of unpaired electron. Under alternating magnetic field at GHz, the electronic transition from the lower energy state to the higher one is expected to attenuate microwave energy intensely, which is known as electron paramagnetic resonance (EPR) [45,46]. Besides, the five d -orbitals of transition metals in HE TMB_2 under a combination of coulombic attraction and bonding interactions are expected to go through energy-level splitting. The crystal field-splitting energy is tunable by adjusting the metal ion, and the interconversion between different energy levels responding to electromagnetic field or heat will also lead to considerable permeability [47]. Last but not least, in addition to tunable EM parameters [47–50], the construction of HE TMB_2 will also display a host of unexpected properties including better high-temperature stability [51–53], better oxidation resistance [54], and improved resistance to corrosion and environmental attack [55]. Therefore, it is promising to realize highly efficient and broadband EM wave absorption in HE TMB_2 with good thermal stability, good oxidation, and corrosion resistance.

Aiming at realizing dielectric and magnetic losses coupling and tuning the impedance match through forming high-entropy ceramics, three HE TMB_2 s including $(\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Nb}_{0.25}\text{Ta}_{0.25})\text{B}_2$, $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2$, and $(\text{Cr}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{B}_2$ are designed as new EM wave absorbing materials, which henceforward are referred to HE TMB_2 -1, HE TMB_2 -2, and HE TMB_2 -3, respectively. The selection of transition metal elements in HE TMB_2 s is due to the following considerations. Firstly, TMB_2 s (TM = Ti, Zr, Hf, Nb, Ta, Cr) exhibit the same hexagonal crystal structure. Secondly, the

utilizations of magnetic anisotropy, defect electron spin resonance, and *d*-orbitals splitting features in TMB₂s (TM = Ti, Zr, Hf) contribute to the magnetic loss. Thirdly, the effects of incorporating nonmagnetic TiB₂ and antiferromagnetic CrB₂ on EM wave absorption performance are investigated. Fourthly, the coupling effects of dielectric and magnetic losses are expected considering dual electromagnetic properties, i.e., tailored balance between permittivity and permeability. Fifthly, except for CrB₂, TMB₂s (TM = Ti, Zr, Hf, Nb, Ta) possess high melting point around 3000 °C, while the existence of Cr element is beneficial to form a protective Cr₂O₃ layer and improve oxidation resistance. Therefore, the formation of HE TMB₂ could lead to further improvement of overall properties including thermal stability, oxidation and corrosion resistance, and EM wave absorption performance.

2 Materials and method

2.1 Theoretical investigation on electronic structure and magnetic properties of TMB₂

To elucidate the electronic structure and magnetic properties of TMB₂, first-principles calculations were carried out using density functional theory (DFT) implemented in the Cambridge Serial Total Energy Package (CASTEP) code [56]. In this work, the Vanderbilt-type ultra-soft pseudopotential [57] and generalized gradient approximation (GGA) based on the Perdew–Burke–Ernerhof (PBE) scheme were employed [58]. For all calculations, the plane-wave basis set cutoff energy was 450 eV, and a $10 \times 10 \times 8$ special k-point mesh according to Monkhorst–Pack method [59] was adopted over the Brillouin zone. Geometry optimization was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme [60]. The convergence thresholds for cell optimization are difference on total energy within 5×10^{-6} eV/atom, maximum ionic Hellmann–Feynman force within 0.01 eV/Å, maximum stress within 0.02 GPa, and maximum ionic displacement within 5×10^{-4} Å. To evaluate the bonding nature of TMB₂, Mulliken population analysis [61,62] was carried out with a constant basis set. To investigate the magnetic properties of CrB₂, spin-polarized calculations were performed on CrB₂ [63]. Besides, the calculations of projected density of states were performed using a projection of the plane-wave electronic states onto a localized linear

combination of atomic orbitals (LCAO) basis set. To study the effects of incorporating CrB₂ into TiB₂ without non-full *d* subshell, spin-polarized calculations were performed on (Ti_{1-x}Cr_x)B₂ (*x* = 0, 0.25, 0.5, 0.75) solid solutions, where $2 \times 2 \times 1$ supercells were used.

2.2 Synthesis of HE TMB₂ powders

To investigate the EM wave absorption performance of HE TMB₂, three HE TMB₂s were designed and then synthesized by boro/carbothermal reduction (BCTR) approach according to Reactions (1)–(3):

Transition metal oxides (TiO₂, Cr₂O₃, ZrO₂, HfO₂, Nb₂O₅, Ta₂O₅, 99.9% purity, 1 μm; China New Materials Technology Co., Ltd., Beijing, China) and B₄C powders (98% purity, −200 mesh; Mudanjiang Qianjin Reagent Co., Ltd., Heilongjiang, China) were used as the starting reactants. Considering the evaporation of boron oxides (i.e., B₂O₃ and BO) at high temperature in vacuum, 10 wt% excess B₄C was added to compensate for the loss of boron source [64].

For the synthesis of HE TMB₂ powders, the starting reactants with the molar ratio of transition metal oxides and boron-carbide powders listed in Table 1 were weighted and thoroughly mixed in an agate mortar. The mixed powders were uniaxially pelletized in a stainless-steel die to obtain cylindrical pellets of 12 mm in diameter. The pellets were then calcined at 1950 °C for 1 h in vacuum. Finally, the as-prepared pellets were crushed, grounded in an agate mortar, and then sieved through a 120-mesh screen for subsequent characterizations.

Table 1 Constituent of raw materials used for synthesizing HE TMB₂ powders

HE TMB ₂	Molar ratio of the raw reactant
HE TMB ₂ -1	ZrO ₂ : HfO ₂ : Nb ₂ O ₅ : Ta ₂ O ₅ : B ₄ C = 2 : 2 : 1 : 1 : 6.6
HE TMB ₂ -2	TiO ₂ : ZrO ₂ : HfO ₂ : Nb ₂ O ₅ : Ta ₂ O ₅ : B ₄ C = 2 : 2 : 2 : 1 : 1 : 8.17
HE TMB ₂ -3	Cr ₂ O ₃ : ZrO ₂ : HfO ₂ : Nb ₂ O ₅ : Ta ₂ O ₅ : B ₄ C = 2 : 2 : 2 : 1 : 1 : 8.01

2.3 Characterization

Phase composition was analyzed by an X-ray diffractometer (XRD; D8 Advanced, Bruker, Germany) utilizing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) with a step size of 0.02° at a scanning rate of $2^\circ/\text{min}$. The final elemental composition was examined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5800, USA). To obtain the lattice parameter, Rietveld refinement was performed using the total pattern solution software (TOPAS; Bruker Corp., Karlsruhe, Germany). The microstructure of as-prepared HE TMB₂ powders was investigated by a scanning electron microscope (SEM; Apollo 300, CamScan, UK) equipped with an energy dispersive spectroscopy system (EDS; Inca X-Max 80 T, Oxford, UK). The particle diameter distributions were analyzed based on the secondary electron images, of which at least 350 particles were counted by Feret's statistical method [65]. The distributions of TM elements were investigated by a (scanning) transmission electron microscope ((S)TEM; JEOL JEM 2100F, 200 kV, Japan) equipped with an 80 mm silicon drift energy dispersive X-ray spectroscope (EDS) and a high-angle annular dark field (HAADF) detector.

The relative complex permittivity ($\varepsilon_r = \varepsilon' + j\varepsilon''$) and permeability ($\mu_r = \mu' + j\mu''$) were determined by a vector network analyzer (Agilent N5244A, USA) using the coaxial method in the frequency range of 1.0–18.0 GHz. HE TMB₂ powders and paraffin wax were mixed at a mass ratio of 7 : 3 and compacted into a toroidal shape ($\Phi_{\text{out}} = 7.00 \text{ mm}$, $\Phi_{\text{in}} = 3.04 \text{ mm}$). Based on the transmission-line theory and metal back-panel model, the RL was determined from the relative complex permittivity and permeability for a given frequency and sample thickness according to the following equations [4,33]:

$$\text{RL(dB)} = 20 \log |(Z_{\text{in}} - Z_0)/(Z_{\text{in}} + Z_0)| \quad (4)$$

$$Z_{\text{in}} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left(j \frac{2\pi f d \sqrt{\mu_r \varepsilon_r}}{c} \right) \quad (5)$$

where Z_0 represents the impedance of free space, Z_{in} represents the normalized input characteristic impedance at the interface between atmosphere and absorber, μ_r is the relative complex permeability, ε_r is the relative complex permittivity, f is the frequency, d is the thickness of samples, and c is the velocity of light ($3 \times 10^8 \text{ m/s}$). The EAB is defined by the frequency range over which the RL value is smaller than -10 dB , which is comparable to 90% microwave energy absorption [33].

3 Results and discussion

The AlB₂-type structure is shown in Fig. 1, which is designated as C32 with the space group of $P6/mmm$ (No. 191) [41]. In this crystal structure, the graphite-like boron layers alternate with the closed packed metal layers, forming a quasi-layered structure.

3.1 Electronic structure and magnetic properties of TMB₂ (TM = Ti, Zr, Hf, Nb, Ta, Cr)

As a result of charge transferring and interactions between TM and B atoms, TM–B bonding is ionic-covalent. To determine the ionicity of TM–B bonding, Table 2 summarizes the results of Mulliken population analysis. All calculations are based on a consistent atomic basis set to yield Mulliken charge and overlap population for qualitative comparison, whose reliabilities are ensured by spilling parameters in the order of 10^{-3} or less. Relatively larger Mulliken charge and relatively smaller overlap population indicate a larger ionic degree of TM–B bonding [61,62]. Therefore, the ionicity of TMB₂ shows a decreasing tendency with the increased number of electronic shell and valence electron, i.e., the ionic binding ability decreases from 3d to 5d TMB₂

Fig. 1 Crystal structure of TMB₂, wherein alternating sheets of TM atoms (dark red) and boron atoms (gray blue) form a quasi-layered structure.

Table 2 Spilling parameters, Mulliken charge, and overlap populations (TM–B bond population and B–B bond population) calculated by Mulliken population analysis

TMB ₂	Spilling parameter	Cation charge (e)	TM–B bond population	B–B bond population
TiB ₂	1.2×10^{-3}	1.10	0.12	2.39
ZrB ₂	1.1×10^{-3}	1.14	0.15	2.40
HfB ₂	5.0×10^{-4}	1.05	0.38	2.24
NbB ₂	1.5×10^{-3}	1.00	0.19	2.27
TaB ₂	9.0×10^{-4}	0.99	0.32	2.09
CrB ₂	1.0×10^{-3}	0.91	0.14	1.71

and weakens with increasing valence electrons, which is derived from the enhanced hybridization between TM d and B p electrons [30,31,66]. Therefore, it is expected that TiB_2 possesses the highest degree of ionicity among the group of TMB_2 .

Spin-polarized calculations were performed to investigate the magnetic properties [63]. Figures 2(a) and 2(b) show the energy band and spin density of states of CrB_2 , respectively, in which energy splitting and partially polarized spins are observed. The elimination of degeneracy in spin-up (α) and spin-down (β) eigenstates especially in the vicinity of Fermi states accounts for the high Pauli spin susceptibility, which is due to the reorientation of high energy electrons with reverse spin direction as a respond to the external magnetic field [67]. According to the magnetic susceptibility calculation by Grechnev *et al.* [42], CrB_2 exhibits the largest magnetic susceptibility among group 4 to group 6 TMB_2 , to which Pauli spin susceptibility makes almost the fully contribution. Apart from the existence of partially polarized spins, the Cr d -orbital splitting due to crystal field effect could also result in different energy states. As shown in Figs. 2(c) and 2(d), the splitting of d orbitals leads to lower energy Cr e_g orbitals and high energy Cr t_{2g} orbital, which is opposite to the energy splitting scenarios of transition metal carbides due to divergent ligand environment [47]. Therefore, incorporating CrB_2 into HE TMB_2 is expected to exhibit high permeability due to the high magnetic susceptibility and the d -orbital splitting.

Unlike CrB_2 , TMB_2 (TM = Ti, Zr, Hf, Nb, Ta) without non-full d subshell exhibit no spin polarized phenomenon, while d -orbital splitting effects are commonly observed. Representative band structure and partial density of states of TiB_2 are displayed in Figs. 3(a) and 3(b). The density of states near Fermi level is contributed by Ti $3d$ and B $2p$, which endows TiB_2 good electrical conductivity. The charge density near Fermi level in Fig. 3(c) shows Ti $3d(e_g)$ orbitals, while that with higher energy in Fig. 3(d) exhibits Ti $3d(t_{2g})$ orbitals. Under the external magnetic field, the energy level transition between Ti $3d(e_g)$ and Ti $3d(t_{2g})$ might lead to magnetic loss.

As shown in Fig. 4, TiB_2 without unpaired electrons exhibits no spin polarization. To investigate the effects of the incorporation of CrB_2 into TiB_2 , spin-polarized calculations were performed on $(\text{Ti}_{1-x}\text{Cr}_x)\text{B}_2$ ($x = 0, 0.25, 0.5, 0.75$) solid solutions, where $2 \times 2 \times 1$ supercells were used. Notably, the total spin density of states of TiB_2 , $(\text{Ti}_{0.75}\text{Cr}_{0.25})\text{B}_2$, $(\text{Ti}_{0.5}\text{Cr}_{0.5})\text{B}_2$, and $(\text{Ti}_{0.25}\text{Cr}_{0.75})\text{B}_2$ at Fermi level are 0, 0.58, 0.43, and 2.21, respectively, indicating that the introduction of CrB_2 will spur partial spin polarization and magnetic susceptibility. Similar results were obtained when CrB_2 was introduced into other TMB_2 (TM = Zr, Hf, Nb, Ta). Therefore, incorporating magnetic CrB_2 into HE TMB_2 is meaningful for tuning the EM parameters, i.e., decreasing the electrical conductivity and increasing the magnetic loss capability in the meantime, thus leading to better impedance match and excellent EM wave absorption performance.

Fig. 2 (a) Electronic structure and (b) spin density of states of CrB_2 ; (c) low energy e_g and (d) high energy t_{2g} levels.

Fig. 3 (a) Electronic structure and (b) partial density of states of TiB_2 ; (c) low energy e_g and (d) high energy t_{2g} levels.

Fig. 4 Spin density of states of (a) TiB_2 , (b) $(\text{Ti}_{0.75}\text{Cr}_{0.25})\text{B}_2$, (c) $(\text{Ti}_{0.5}\text{Cr}_{0.5})\text{B}_2$, and (d) $(\text{Ti}_{0.25}\text{Cr}_{0.75})\text{B}_2$, where $2 \times 2 \times 1$ supercells were used.

3.2 Synthesis and characterization of HE TMB₂ powders

From Fig. 5, the XRD patterns of three as-synthesized HE TMB₂s reveal that the main reflection peaks are indexed as AlB_2 -type phase, indicating that the HE TMB₂ with multi-principal TM elements were formed

after synthesized at 1950 °C for 1 h. Minor impurities including unsolved AlB_2 -type TMB₂ (TM = Zr, Hf) and Ta_3B_4 -type orthorhombic TM_3B_4 solid solutions are also detected in HE TMB₂-1 (TM = Zr, Hf, Nb, Ta) and HE TMB₂-2 (TM = Ti, Zr, Hf, Nb, Ta). In specific, minor peaks assigned to the (001) and (101) planes are indexed as TMB₂ (TM = Zr, Hf), indicating that the

Fig. 5 XRD patterns of HE TMB₂-1 (TM = Zr, Hf, Nb, Ta), HE TMB₂-2 (TM = Ti, Zr, Hf, Nb, Ta), and HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta) synthesized at 1950 °C for dwelling time of 1 h.

formation of solid solution is a multi-step procedure due to the different mutual diffusivity of TM elements. From the thermodynamic perspective, the favorable temperature for synthesizing TMB₂ according to Reactions (1)–(3) increases in an order of TaB₂, NbB₂, TiB₂, ZrB₂, and HfB₂ [64]. Therefore, the deferred reductions of ZrO₂ and HfO₂ are responsible for the insufficient solid solution formation. Besides, the presence of TM₃B₄ solid solution phases indexed in the vicinity of (100) peak is mainly attributed to two factors, namely, the accelerated volatilization of boron oxide at high temperature and good thermodynamic stability of TM₃B₄ (TM = Ti, Nb, Ta) [68]. Compared with the synthesis results conducted by Gu *et al.* [64], the evaporation of boron oxides at 1950 °C is more severe, leading to the insufficient boron source. The presence of minor impurities has no detrimental effects on the EM absorption performance [48]. Notably, only AlB₂-type reflections can be detected in as-synthesized HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta), which is structurally ordered but compositionally disordered with multi-principal TM elements. As shown in Fig. 6, the peak positions of HE TMB₂-3 are lying in the middle of those of single components TMB₂ (TM = Zr, Hf, Nb, Ta), while keeping a distance from those of

Fig. 6 XRD patterns of HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta) powders together with those of CrB₂, ZrB₂, HfB₂, NbB₂, and TaB₂ obtained from ICDD/JCPDS cards.

CrB₂, which could be ascribed to the limited solid solution quantity of CrB₂ with relatively smaller lattice parameters.

The final compositions of multi-principal TM elements are of significance for the EM wave absorption performance. Table 3 compares the nominal equimolar compositions and the elemental compositions analyzed by ICP-OES. The elemental proportions of TM cations examined by ICP-OES in HE TMB₂-1 and HE TMB₂-2 are close to equimolar, while the atomic content of Cr is lower than those of the other TM elements in HE TMB₂-3, which is responsible for the offset of the reflection peaks in Fig. 6. Therefore, combining XRD and ICP-OES analyses, the final composition of HE TMB₂-3 is determined as (Cr_{0.139}Zr_{0.210}Hf_{0.219}Nb_{0.216}Ta_{0.216})B₂. Since the volatility of Cr₂O₃ under vacuum condition has at least three orders of magnitude greater than those of other TM oxides (TM = Zr, Hf, Nb, Ta) used as reactants, the limited solid solution quantity of CrB₂ in HE TMB₂-3 could be ascribed to the evaporation of

Table 3 Nominal compositions and measured elemental compositions of TM in as-synthesized HE TMB₂-1 (TM = Zr, Hf, Nb, Ta), HE TMB₂-2 (TM = Ti, Zr, Hf, Nb, Ta), and HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta)

HE TMB ₂	Nominal composition	Measured composition
HE TMB ₂ -1	(Zr _{0.25} Hf _{0.25} Nb _{0.25} Ta _{0.25})B ₂	(Zr _{0.240} Hf _{0.248} Nb _{0.258} Ta _{0.254})B ₂
HE TMB ₂ -2	(Ti _{0.2} Zr _{0.2} Hf _{0.2} Nb _{0.2} Ta _{0.2})B ₂	(Ti _{0.187} Zr _{0.198} Hf _{0.206} Nb _{0.204} Ta _{0.205})B ₂
HE TMB ₂ -3	(Cr _{0.2} Zr _{0.2} Hf _{0.2} Nb _{0.2} Ta _{0.2})B ₂	(Cr _{0.139} Zr _{0.210} Hf _{0.219} Nb _{0.216} Ta _{0.216})B ₂

Cr₂O₃ with increasing temperature, which is in turn beneficial to boosting the mass transferring [69].

Based on the ICP-OES results, the average lattice parameters ($\bar{a}$, $\bar{c}$) of HE TMB₂s are calculated using the data of TMB₂s derived from the standard ICDD/JCPDS cards. The lattice parameters (a , c) of as-prepared HE TMB₂s were determined by Rietveld refinement using TOPAS software. The theoretical density (ρ) was calculated from the refined lattice parameters and the atomic mass according to the ICP-OES results. Table 4 summarizes the refined lattice parameters (a , c), the average lattice parameters ($\bar{a}$, $\bar{c}$), and the theoretical density (ρ) together with the reliability factors (R_p , R_{wp}). The lattice parameters of HE TMB₂s are close to the average ones, while relatively large deviations of the refined lattice parameters from the average ones ($\Delta a = 0.16\%$, $\Delta c = 1.46\%$) are identified in HE TMB₂-3.

Figures 7(a)–7(c) display representative SEM analyses of as-synthesized HE TMB₂ powders. Under different growth conditions, plate-like and column-like particles with residue growth steps are commonly observed [70].

Figures 7(d)–7(f) display the particle size distribution of as-synthesized HE TMB₂ powders, where HE TMB₂-3 exhibits wide distribution range from 0.5 to 4.2 μm . The average particle size of HE TMB₂-1 and HE TMB₂-2 are 0.83 and 0.78 μm , respectively, while that of HE TMB₂-3 reaches 2.2 μm . The as-synthesized HE TMB₂-1 and HE TMB₂-2 with relatively smaller particle size of 0.83 and 0.78 μm are expected to exhibit stronger interfacial polarization, which is helpful to boost the dielectric loss.

To characterize the distribution of different TM elements, a representative STEM-EDS analysis of HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta) is shown in Fig. 8. Homogeneous elemental distributions of TM cations both in the grain interior (Fig. 8(a)) and the grain boundary (Fig. 8(b)) are verified by EDS elemental mappings. Combining the XRD and STEM-EDS analyses, it can be concluded that single phase (Cr_{0.139}Zr_{0.210}Hf_{0.219}Nb_{0.216}Ta_{0.216})B₂ (HE TMB₂-3) powders with a homogeneous elemental distribution are synthesized.

Table 4 Refined lattice parameters (a , c), average lattice parameters ($\bar{a}$, $\bar{c}$) from corresponding single component phases obtained from standard ICDD/JCPDS cards, and calculated theoretical density (ρ) together with reliability factors (R_p and R_{wp}) of as-synthesized HE TMB₂s

HE TMB ₂	a (Å)	$\bar{a}$ (Å)	c (Å)	$\bar{c}$ (Å)	ρ (g/cm ³)	R_p (%)	R_{wp} (%)
HE TMB ₂ -1	3.1267	3.1295	3.3950	3.3737	9.110	11.87	15.92
HE TMB ₂ -2	3.1065	3.1113	3.3738	3.3473	8.335	9.10	12.30
HE TMB ₂ -3	3.1031	3.1081	3.3825	3.3337	8.610	8.37	11.23

Fig. 7 SEM images and particle distributions of (a, d) HE TMB₂-1 (TM = Zr, Hf, Nb, Ta), (b, e) HE TMB₂-2 (TM = Ti, Zr, Hf, Nb, Ta), and (c, f) HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta) powders synthesized at 1950 °C for the dwelling time of 1 h.

Fig. 8 Representative STEM images in (a) the grain interior and (b) the grain boundary and the corresponding EDS elemental mappings.

3.3 Electromagnetic properties of HE TMB₂ powders

Generally, the dissipations of EM wave energy can be conducted by electronic and/or magnetic interactions between microwave absorbers and alternating EM wave field. Therefore, complex permittivity ($\varepsilon_r = \varepsilon' + j\varepsilon''$) and complex permeability ($\mu_r = \mu' + j\mu''$) are two critical factors determining the EM wave absorption performance, of which the real parts (ε' and μ') and the imaginary parts (ε'' and μ'') represent the storage and loss capabilities of EM wave energy, respectively [33].

To assess the EM wave absorption performance of as-synthesized HE TMB₂ powders, the frequency dependent EM parameters are summarized in Fig. 9. As revealed in Fig. 9(a), the values of ε' decrease with increasing frequency as a phenomenon of dispersion and exhibit distinctions among three HE TMB₂s, indicating that the dielectric polarization ability ranks in the following order: HE TMB₂-2 > HE TMB₂-1 > HE TMB₂-3. In essence, the polarizability of dielectric medium is made up of several contributions from electronic polarization, ionic polarization, orientational polarization, and space charge polarization [71]. The relaxation frequencies of electronic and ionic deviation polarizations are in the frequency range of THz and PHz, respectively, which can keep shifting orientation direction with alternating electric field at GHz range. However, space charge polarization fails to make contribution due to its low relaxation frequency, while the effect of orientational polarization is reduced with increasing frequency. Therefore, electronic and ionic deviation polarizations play a dominant role in

determining the polarizability, while orientational and space charge polarizations contribute to the dielectric loss. As for TMB₂s, the ionic-covalent TM–B bonding consists of ionic bonding due to charge transferring from TM atom to B atom and covalent bonding from the hybridization between TM *d* and B *p* electrons. From 3*d* to 5*d* TMB₂, the TM–B ionic binding ability becomes weaker as is reflected by the reduced Mulliken charge and increased TM–B bond population in Table 2. In this light, Ti–B bonding exhibits the largest degree of ionic bonding and the smallest ionic mass, which is expected to possess the strongest ionic polarizability. As for electronic polarization, Ti 3*d* electrons are strictly localized and possess the strongest Coulomb interaction compared with other delocalized TM *d* electrons, which reinforces the restoring force and is beneficial to strengthening electronic polarization. Therefore, the incorporation of TiB₂ into HE TMB₂-2 is beneficial to strengthening the dielectric storage capability. Figure 9(b) shows the frequency dependence of imaginary permittivity (ε''), which is mainly derived from polarization relaxation loss and conduction loss, and can be described as [33]:

$$\varepsilon'' \approx \varepsilon_p'' + \varepsilon_c'' = (\varepsilon_0 - \varepsilon_\infty) \frac{\omega\tau}{1 + \omega^2\tau^2} + \frac{\sigma}{2\pi f \varepsilon_0} \quad (6)$$

where ε_p'' and ε_c'' represent the polarization loss and conduction loss, respectively, ε_0 and ε_∞ refer to the permittivity in vacuum and at infinite frequency, respectively, ω is the angular frequency, τ is the relaxation time, and f is the frequency. The presence of residue impurities and paraffin wax can spur the interfacial polarizations (called the Maxwell–Wagner effect [72]) and related relaxations in heterogeneous materials, which is related to the specific surface area

Fig. 9 Electromagnetic parameters of HE TMB₂s: (a) real permittivity (ϵ'), (b) imaginary permittivity (ϵ''), (c) real permeability (μ'), and (d) imaginary permeability (μ'').

of HE TMB₂ powders. The average particle size of HE TMB₂-1 and HE TMB₂-3 differs by a factor of about 3. However, their ϵ'' values distinct scarcely, which indicates that there are other dominant pathways to dissipate EM wave energy rather than interfacial polarization loss. According to the free electron theory [33] ($\epsilon''_c = \sigma / (2\pi f \epsilon_0)$), the reduction of electric conductivity (σ) will lead to the reduction of the ϵ'' value. With the increase of disorder in a fixed lattice assessed by configurational entropy (ΔS_{conf}), the electrical conductivity decreases in the order of HE TMB₂-1, HE TMB₂-3, and HE TMB₂-2, which coincides with the decreased magnitude of ϵ'' . Therefore, it can be concluded that the conduction loss is the dominant contributor for the dielectric loss. Besides, the formation of solid solution with multi-principal components is expected to introduce a host of defects, which could serve as polarization centers and hinder the re-orientation of dipoles and the rearrangement of space charges in the alternating electric field, thus leading to energy consumption. Therefore, multi-relaxations in GHz range are responsible for the resonance peaks existing in the ϵ'' - f curves for HE TMB₂s.

Generally, the dielectric loss ability can be evaluated by dielectric loss tangent ($\tan \delta_\epsilon = \epsilon'' / \epsilon'$). As shown in

Fig. 10(a), HE TMB₂-1 and HE TMB₂-3 exhibit similar magnitude of dielectric loss across the testing frequency span, while HE TMB₂-2 possesses relatively lower loss tangent values. As mentioned above, except for conduction loss, polarization relaxation loss also contributes to the dielectric loss, which can be determined by Cole–Cole curves in Fig. 10(c). Due to the unneglectable conductivity and multi-relaxation time existing in HE TMB₂s, the skewed semicircles are identified, which represent relaxation progresses [33].

The complex permeability and magnetic loss tangent of HE TMB₂s are shown in Figs. 9(c), 9(d), and 10(b). In Fig. 9(c), the μ' values of HE TMB₂s gradually decrease with increasing frequency due to the relaxations of magnetic moments. Notably, the incorporation of TiB₂ in HE TMB₂-2 gives rise to the reduction of μ' values over the testing frequency span compared with HE TMB₂-1, which is related to the diamagnetism induced by the localized Ti 3d electrons [42,73]. As for HE TMB₂-3, the antiferromagnetic CrB₂ possesses the highest magnetic susceptibility among group 4 to group 6 TMB₂s due to partially polarized spins, which is critical for the enhancement of magnetic storage capacity [42–44]. In Fig. 9(d), the μ'' values of HE TMB₂-1 and HE TMB₂-3 exhibit decreasing tendency with frequency, while for HE TMB₂-2, the μ'' values increase from 1 to 5 GHz and decrease in the frequency

Fig. 10 Frequency dependences of (a) dielectric loss tangent ($\varepsilon''/\varepsilon'$) and (b) magnetic loss tangent (μ''/μ'); (c) Cole–Cole semicircles (ε'' vs. ε') and (d) C_0 - f curves of HE TMB₂s.

range of 5–14 GHz and then keep almost steady above 14 GHz. Thus, the incorporation of TiB₂ into HE TMB₂-2 can refrain from the skin effect occurred in HE TMB₂-1 and realize better impedance matching at high frequency, as demonstrated by the positive values of μ'' in frequency range of 14–18 GHz [6,7]. Moreover, the μ'' values of HE TMB₂-3 with antiferromagnetic CrB₂ remain a high level in the frequency range of 1–18 GHz, which is beneficial to high magnetic loss. As is expected, obvious resonance peaks of magnetic loss tangent ($\tan \delta_\mu = \mu''/\mu'$) are observed, which could be ascribed to the resonance loss in Fig. 10(b). Under the weak EM field at GHz range, the electron paramagnetic resonance frequency is at microwave frequency range, which is expected to cause intense attenuation of EM wave energy [45,46]. Besides, the excitation from different d -orbital energy levels as a respond to incident EM wave energy also contributes to resonance loss [47]. Therefore, the resonance loss and eddy current loss are the dominant contributors to the magnetic loss, wherein the eddy current loss is only related to the electrical conductivity (σ) of materials and the matching thickness (d), as described by Eq. (7) [33]:

$$C_0 = \mu''(\mu')^{-2} f^{-1} = 2\pi\mu_0 d^2 \sigma \quad (7)$$

where μ_0 is the vacuum permeability. Supposing that the eddy current loss is the sole reason for the magnetic loss, the value of C_0 should remain a constant; otherwise, the electron paramagnetic resonance loss is preponderance. As shown in Fig. 10(d), in spite of the unchanged period of the C_0 - f curve from 14 to 18 GHz for HE TMB₂-2, the C_0 values of HE TMB₂s exhibit apparent variation with frequency, indicating electron paramagnetic resonances occur in the testing frequency range. From Fig. 10(b), the resonance frequency for HE TMB₂-1, HE TMB₂-2, and HE TMB₂-3 are 9.2, 5.1, and 9.8 GHz, respectively. The occurrences of resonance loss at GHz range are mainly attributed to the anisotropic magnetic susceptibility, crystal field effects, as well as electron paramagnetic resonance induced by a host of defects in HE TMB₂s.

Combining dielectric and magnetic loss tangents, it can be inferred that the synergistic effects of dielectric and magnetic losses are realized in three HE TMB₂s, which are expected to display high EM wave absorption performance. Figure 11(a) exhibits the total loss tangent ($\tan \delta_\varepsilon + \tan \delta_\mu$) of HE TMB₂s, indicating that the consumption capacity of EM wave energy could be ranked roughly in the following order: HE TMB₂-3 > HE TMB₂-1 > HE TMB₂-2. Taking the coupling

Fig. 11 Frequency dependences of (a) total loss tangent ($\tan\delta_e + \tan\delta_\mu$) and (b) attenuation constant (α); comparison of (c) RL values and (d) impedance match (Z_{in}/Z_0) of HE TMB₂s.

effects of dual losses into account, the attenuation constant (α) is used for a comprehensive comparison of the dissipation capability of HE TMB₂s according to Eq. (8) [7]:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}} \quad (8)$$

As shown in Fig. 11(b), the α values of HE TMB₂-1 and HE TMB₂-3 are comparable, and both are larger than those of HE TMB₂-2 below 14 GHz but are exceeded by HE TMB₂-2 above 14 GHz, indicating that three HE TMB₂s exhibit frequency dependent dissipation capability. To assess the EM wave absorption performance, RL as a critical criterion is simulated by Eqs. (4) and (5). As depicted in Fig. 11(c), at the same thickness of 2.5 mm, HE TMB₂-1 and HE TMB₂-3 exhibit good EM wave absorption capacity at X band (8–12 GHz), while the RL_{min} value of HE TMB₂-2 is considerably smaller, which is ascribed to two main factors, namely, the weaker coupling losses and the poorer impedance match. The impedance match is determined by Z (Z_{in}/Z_0) values. When the Z value is close to 1, it implies better impedance match,

otherwise the EM wave tends to be reflected on the surface of microwave absorbers. As displayed in Fig. 11(d), at the same thickness of 2.5 mm, the Z values of HE TMB₂-1 and HE TMB₂-3 are equal to 1 across a wide frequency range, indicating their ideal impedance matching, while those of HE TMB₂-2 are relatively distant from 1. Notably, as a result of strong dissipation capability and ideal impedance matching, with the thickness of 2.5 mm, the minimum reflection loss (RL_{min}) and EAB of HE TMB₂-1 and HE TMB₂-3 are -37.5 dB, 7.1 GHz and -34.8 dB, and 10.0 GHz, respectively. It is worth noting that HE TMB₂-1 and HE TMB₂-3 exhibit wide effective absorption bandwidth, which is ascribed to ideal impedance match over a wide frequency range.

According to Eqs. (4) and (5), the thickness of microwave absorbers (d) also has impacts on the RL and Z values. Thus, Fig. 12 plots the Z and RL contour maps of HE TMB₂s related to the thickness (d) and frequency (f). It is found that strong absorption capacities are realized in HE TMB₂s, and the optimal RL_{min} values at matching frequency and thickness of HE TMB₂-1, HE TMB₂-2, and HE TMB₂-3 are -59.6 dB (8.48 GHz, 2.68 mm), -47.2 dB (16.9 GHz, 4.40 mm), and -56.2 dB (8.48 GHz, 2.63 mm),

Fig. 12 Contour maps of RL and impedance match (Z) values of (a, b) HE TMB₂-1, (c, d) HE TMB₂-2, and (e, f) HE TMB₂-3.

respectively, when Z values are close to 1. Moreover, it can be concluded that the impedance matching can be tailored by compositional design, as a direct result of adjustable electromagnetic parameters in Fig. 9. In specific, compared with HE TMB₂-1, the incorporation of CrB₂ into HE TMB₂-3 greatly improves the impedance match over the testing frequency span, which is helpful to obtain strong and broadband absorbing capability, while the introduction of TiB₂ in HE TMB₂-2 results in the opposite effects. To elaborate the effects of impedance matching on the effective absorption bandwidth, based on the definition of effective bandwidth, we can conclude that the effective absorption occurs when $0.52 \leq Z \leq 1.93$ by solving Eq. (9) [6]:

$$RL = 20 \log |(Z_{in} - Z_0)/(Z_{in} + Z_0)| \leq -10 \text{ dB} \quad (9)$$

Drawn from the comparison of Z and RL contour

maps in Fig. 12, it is found that the effective absorption areas of HE TMB₂s locate within the regions where $0.52 \leq Z \leq 1.93$. According to the quarter-wavelength model [47]:

$$d_m = \frac{nc}{4f_m \sqrt{|\epsilon_r| |\mu_r|}} \quad (10)$$

where d_m is the matching thickness, $n = 1, 3, 5, \dots$, and f_m is the matching frequency. Obviously, the matching thickness of microwave absorbers tends to decrease when the f_m elevates. Notably, the boosting magnetic loss capability in HE TMB₂-3 especially in the high frequency range as shown in Fig. 10(b) leads to better impedance matching, which is of great significance because the matching thickness can be effectively reduced at high frequencies. As proven in Figs. 12(a)–12(d), the absences of effective absorption with

thin thickness in HE TMB₂-1 and HE TMB₂-2 are ascribed to impedance mismatch at high frequency ranges, while wide effective absorption is achieved in HE TMB₂-3 due to the improved impedance matching in Figs. 12(e) and 12(f). Besides, the effective absorptions at high frequency (14–18 GHz) with thickness above 4 mm in HE TMB₂s are identified, which occur when good impedance match is realized with cancellation series n equal to 3. Moreover, the strong absorption (RL = −47.2 dB) in HE TMB₂-2 at 16.9 GHz with a thickness of 4.48 mm is resulted from synergistic effects of strong attenuation capability (α) and good impedance matching (Z) as shown in Figs. 11(b) and 12(d). From Figs. 12(a), 12(c), and 12(e), the optimal effective absorption bandwidth and the corresponding matching thickness of HE TMB₂-1, HE TMB₂-2, and HE TMB₂-3 are 7.6 GHz (at 2.3 mm), 3.6 GHz (at 2.7 mm), and 11.0 GHz (at 2.2 mm), respectively. In detail, effective absorption (RL < −10 dB) can be realized in HE TMB₂-3 at frequency range of 4–18 GHz by tuning the thickness within 1.5–5 mm, which covers the total C band (4–8 GHz), X band (8–12 GHz), and Ku band (12–18 GHz). To illustrate the superior EM wave absorption performance of HE TMB₂s, Fig. 13 summarizes the optimized EAB and RL values of three HE TMB₂s and some currently reported EM wave absorbers of sulfides based (CF@MoS₂ [6], MoS₂ [12]), MXenes (Ti₃C₂ [14]), ferrites (Fe₃O₄ [15], C@BaMg_{0.2}Co_{0.8}TiFe₁₀O₁₉ [16], Ba_{0.8}La_{0.2}Co_{0.9}Zn_{1.1}Fe₁₆O₂₇ [17]), metal and alloys (Fe [18], FeCo [19], CoNi [20]), carbides (HfC/SiC [25],

HfC [47], TaC [47]), and high-entropy borides (HE REB₆ [49], HE REB₆/HE REBO₃ [49], HE REB₆/HE REB₄ [50]). It is worth mentioning that the EM wave absorbers locating in lower-right corner in Fig. 13 are the target of many investigations, where stands HE TMB₂-1 and HE TMB₂-3. It can be seen that HE TMB₂-1 and HE TMB₂-3 possess the widest EAB and smallest RL values among these EM wave absorbers, demonstrating superior EM wave absorption performance.

Drawn from the above analyses, strong and broadband absorption capability can be achieved by tailoring the impedance matching through designing HE TMB₂s, i.e., the dielectric loss can be adjusted by reducing the electrical conductivity and the magnetic loss can be enhanced by incorporating components with more dissipation pathways of magnetic field energy.

4 Conclusions

In summary, three HE TMB₂ powders with nominal equimolar ratio including HE TMB₂-1 (TM = Zr, Hf, Nb, Ta), HE TMB₂-2 (TM = Ti, Zr, Hf, Nb, Ta), and HE TMB₂-3 (TM = Cr, Zr, Hf, Nb, Ta) were designed and successfully synthesized, which demonstrate promising EM wave absorption performance.

Theoretical calculations based on DFT reveal that TiB₂ possesses the highest degree of ionicity, and CrB₂ exhibits partially polarized spin, while d -orbital splitting effects are commonly observed among TMB₂s. Besides, the introduction of CrB₂ into TiB₂ is helpful to boost the partial spin polarization and the permeability. These features are closely related to the electromagnetic parameters of the as-synthesized HE TMB₂s. XRD analyses indicate that the main phases of AlB₂-type HE TMB₂ with multi-principle TM elements are formed with minor impurities. The final cation composition of HE TMB₂-3 is found distant from the nominal one, which is determined as (Cr_{0.139}Zr_{0.210}Hf_{0.219}Nb_{0.216}Ta_{0.216})B₂ by ICP-OES. Through SEM analysis, plate-like and column-like particles are commonly observed, and the average particle size of HE TMB₂-3 is 2.22 μ m, nearly tripling those of HE TMB₂-1 (0.83 μ m) and HE TMB₂-2 (0.78 μ m). STEM-EDS analysis reveals that the distribution of multiple TM elements in HE TMB₂-3 is homogenous.

As the synergistic effects of the reduced electrical conductivity and the boosted magnetic losses, the target of tuning the balance between dielectric loss and

Fig. 13 Comparison of optimal optimized EAB and RL values of HE TMB₂s and those of current EW wave absorbers.

magnetic loss in single phase HE TMB₂ is achieved, leading to good EM wave absorption performance. The optimal RL_{min} values at matching frequency and thickness of HE TMB₂-1, HE TMB₂-2, and HE TMB₂-3 are −59.6 dB (8.48 GHz, 2.68 mm), −47.2 dB (16.9 GHz, 4.40 mm), and −56.2 dB (8.48 GHz, 2.63 mm), respectively. In addition to strong attenuation capability, broadband absorption capabilities are also demonstrated. The optimal effective absorption bandwidth and the corresponding matching thickness of HE TMB₂-1, HE TMB₂-2, and HE TMB₂-3 are 7.6 GHz (at 2.3 mm), 3.6 GHz (at 2.7 mm), and 11.0 GHz (at 2.2 mm), respectively. The introduction of CrB₂ in HE TMB₂-3 greatly improves the impedance match, thus leading to high efficiency and broadband absorption performance. Considering good thermal stability, oxidation and corrosion resistance, HE TMB₂ ceramics are promising as a new type of EM wave absorbing materials that cater the needs for applications in harsh serving environments.

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