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# Dielectric and electromagnetic wave absorption properties of reduced graphene oxide/barium aluminosilicate glass–ceramic composites

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**Abstract**

$BaAl_2Si_2O_8$ (BAS) glass–ceramic powders were prepared by sol–gel method. Graphene oxide (GO)/BAS mixture powders were prepared by a simple mixing process of GO and BAS. Dense and uniform reduced graphene oxide (RGO)/BAS composites were fabricated by the hot-pressing of GO/BAS, which was accompanied by the in-situ thermal reduction of GO. Microstructure, phase composition, dielectric and electromagnetic wave (EM) absorption properties of RGO/BAS were investigated. The results reveal that RGO can promote the hexacelsian-to-celsian phase transformation of BAS. In the frequency range from 8 GHz to 12 GHz, the complex permittivity of RGO/BAS increases with increasing RGO content. The composite with 1.5 wt% of RGO shows good EM absorbing ability. When the sample thickness is 2.1 mm, the minimum reflection coefficient (RC) reaches −33 dB, and the effective absorption bandwidth is more than 3.1 GHz.


*Keywords:* C. Dielectric properties; D. Glass–ceramic; Phase transformation; Electromagnetic wave absorption

## 1. Introduction

Barium aluminosilicate ($BaAl_2Si_2O_8$, BAS), with the melting point of ~1760 °C, is one of the most refractory glass–ceramics. The monoclinic polymorph of BAS (celsian) has low-thermal expansion coefficient ($2.29\times10^{-6}$/°C from 22 °C to 1000 °C), low and stable dielectric constant ($\varepsilon_r=6.55$–$7.00$, $\tan\delta=0.8\times10^{-3}$–$4.0\times10^{-3}$ at 35 GHz from 25 °C to ~1200 °C) and good oxidation resistance [1–3]. It has been investigated for its potential in applications such as missile radomes, environmental barrier coatings (EBC) and matrices of thermo-structural composites [4–9]. However, in the crystallization process of BAS, the undesirable phase hexacelsian always forms first and hardly transform into celsian [10]. Hexacelsian is the hexagonal polymorph of BAS and is stable above 1590 °C. Hexacelsian has high-thermal expansion coefficient of $8\times10^{-6}$/°C (300–1000 °C) [1,11]. Besides, it transforms into the orthorhombic form at ~300 °C, which is accompanied by a volume change of ~3% to 4%. This structural transformation would result in microcracking of the BAS matrix. Thus, successful employment of BAS requires a previous stabilization of its monoclinic form [12].

Over the past years, several researches relating to the hexacelsian-to-celsian phase transformation of BAS have been done [12–20]. It was reported that the addition of some mineralizers, such as $Li_2O$, MgO, CaO, NaF, and $TiO_2$, could promote the hexacelsian-to-celsian phase transformation [16]. Bansal et al. investigated the kinetics of hexacelsian-to-celsian phase transformation of $BaAl_2Si_2O_8$ and $SrAl_2Si_2O_8$ [13–15]. They revealed that partial substitution of BaO by SrO in polycrystalline BAS could facilitate the hexacelsian-to-celsian phase transformation. Debsikdar et al. revealed that addition of celsian powders as "seeds" could promote hexacelisian-to-celsian transformation during sintering [19].

Various kinds of BAS-based composites, including particulate-, whisker-, platelet- and fiber-reinforced BAS composites, have been extensively investigated [21–32]. Bansal et al.

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fabricated Hi-Nicalon fiber reinforced celsian composites and investigated their mechanical properties after high-temperature exposure in air [21–22]. Ye Feng et al. fabricated a series of BAS-based composites, including $Si_3N_4$ whiskers reinforced BAS composites ($Si_3N_{4w}$/BAS), SiC platelet reinforced BAS composites ($SiC_{pl}$/BAS), carbon short fiber reinforced BAS composites ($C_{sf}$/BAS), carbon nanotube reinforced BAS composites (CNTs/BAS) and α-SiC/β-$Si_3N_4$ co-reinforced BAS composites, and investigated their mechanical properties [26–32]. Among these composites, CNTs/BAS composites exhibited excellent mechanical properties. In addition, it was reported that addition of CNTs could greatly enhance the electrical conductivity and dielectric permittivity of ceramic-based composites [33–34].

In the last decade, owing to the rapidly increasing electromagnetic pollution, electromagnetic wave (EM) absorption materials have aroused great interests. Carbon materials-based composites, especially CNTs-based composites, show the most attractive performance [33–35]. Graphene, the new member of carbon materials family, has emerged as a promising alternative to CNTs in various fields due to its unique electrical, mechanical, thermal properties in addition to light weight and high surface area [36–37]. Together with other carbon materials, graphene has attracted great attentions in EM absorption fields. Numerical studies show that EM absorption materials must have good impedance properties, which mean suitable complex permittivity (e.g., $\varepsilon' = 5–20$, $\varepsilon'' = 1–10$ in 8–12 GHz band) [38]. However, the complex permittivity of pure graphene is too high for EM absorption. Nowadays, low-cost graphene can be produced in bulk through reduction of graphene oxide (GO). Generally, the graphene product obtained by the above method is called reduced graphene oxide (RGO). The complex permittivity of RGO can be modified by the reduction process to meet the requirement of EM absorption. Therefore, RGO is more suitable for EM absorption than pure graphene. The EM absorption properties of RGO-based composites have been extensively investigated and it is revealed RGO-based composites exhibit excellent EM absorbing ability [39–42]. Most of these works focused on nano-particles decorated RGO and their applications are limited by the problems oxidation resistance and high-temperature stability. Fortunately, carbon materials/ceramic composites, including $C_{sf}/SiO_2$, RGO/$SiO_2$, CNTs/$SiO_2$, show excellent performance at high temperatures since ceramics matrix can protect the carbon materials fillers [33,39,43]. Therefore, RGO/ceramic composites may be alternatives for nano-particles decorated RGO in high-temperature environment.

So far, reduced graphene oxide/barium aluminosilicate (RGO/BAS) composites have not been reported. In this study, GO/BAS mixture powders were prepared by a simple mixing process of GO and BAS. RGO/BAS composites were prepared by the hot-pressing of GO/BAS. The reduction of GO occurred together with the composites densification in hot-pressing, thus avoided the severe agglomeration of RGO. As a result, uniform and dense RGO/BAS composites were obtained. The microstructure, phase composition, dielectric and EM absorption properties of RGO/BAS composites were investigated.

## 2. Experimental

### 2.1. Materials preparation

BAS powders were prepared through a sol–gel process. All the chemicals in the experiments were analytical grade reagents. Ethanol, deionized water and tetraethyl orthosilicate (TEOS) with the mole ratio of 4:1:1 were mixed by magnetic stirring, the mixed solution was denoted as solution A. Stoichiometric $BaCO_3$ and $Al(NO_3)_3 \cdot 9H_2O$ were added into 60 wt% citric acid solution, then the solution was kept statically at room temperature until the reaction completed, the obtained solution was denoted as solution B. The solution B was poured into solution A under vigorously stirring. Ammonia was added into the mixed solution very slowly until the solution became clear, and the pH of the mixed solution was ~3 to 4. The clear solution was stirred continuously at room temperature until gelation occurred. The gels were placed at 100 °C for one week to obtain dried gels. The dried gels were treated at 500 °C in static air for 2 h, and then treated at 800 °C for 2 h to remove the residual organics. As a result, non-crystallizing BAS powders were obtained. The as-obtained BAS powders were milled using a planetary ball mill for 12 h to obtain fine powders.

Commercial available graphene oxide (XF002, XF Nano Materials Tech Co., Nanjing) was dispersed in deionized water with the concentration of 0.5 mg/ml via sonication. Appropriate amount of BAS powders were poured into the GO aqueous dispersion. The mixed solution was sonicated for 1 h and vigorously stirred for 12 h. The mixed powders were isolated by vacuum filtration and treated at 60 °C for one week to remove the residual water. As a result, GO/BAS powders were obtained. The mass ratio of GO in GO/BAS was 0, 0.5, 1.0, 1.5, and 2.0 wt%, respectively.

The as-prepared GO/BAS powders were placed into a 50 mm diameter cylindrical graphite die for hot-pressing sintering. The hot-pressing sintering was carried out at 1350 °C for 2 h, with the pressure of 25 MPa. In this process, GO was thermal reduced into RGO. As a result, RGO/BAS glass–ceramic composites were obtained. Due to the removal of functional groups, the mass ratio of RGO in RGO/BAS was lower than that of GO in GO/BAS. For convenience, the as-obtained RGO/BAS composites were also denoted as 0, 0.5, 1.0, 1.5, and 2.0 wt% RGO/BAS composites.

### 2.2. Characterization

The bulk density and porosity were measured by the Archimedes displacement method according to ASTM C-20 standard. The phase composition was identified by X-ray diffractometry (XRD) via a computer-controlled diffractometer (X'Pert Pro, Philips, Netherlands) with Co radiation. The microstructure was observed by a scanning electron microscopy (SEM, S-4700, Hitachi, Japan). Raman spectra were taken on a Renishaw Ramoscope (Confocal Raman Microscope, inVia, Renishaw) equipped with a He–Ne laser ($k = 514$ nm). X-ray photoelectron spectra (XPS) were measured using

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