VO$_2$-dispersed glass: A new class of phase change material

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Energy storage technology is crucial for a sustainable society, and its realization strongly depends on the development of materials. Oxide glass exhibits high durability. Moreover, the amorphous structure of the glass without periodic ordering demonstrates excellent formability and controllability, thus enabling a large-scale production. These factors provide impetus for the development of new materials for thermal management applications. As vanadium dioxide (VO$_2$) with a strongly correlated electron system exhibits a structural phase transition, leading to a large heat of transition. Therefore, VO$_2$ demonstrates immense potential as a phase change material (PCM). This study reports the fabrication of VO$_2$-dispersed glass and examines its potential as a new latent heat storage material, which can be applied for massive PCM heat storage applications.

Heat is known to be a considerable form of energy available in the surrounding environment, e.g., solar-thermal energy and exhaust heat, which are generated by natural and artificial actions, respectively. Thus, heat is a primitive but a crucial form of energy in daily life. Hence, heat storage technology is indispensable for efficient energy utilization and sustainable development. This technology can appropriately balance the supply and demand amounts of thermal energy for different times and/or spaces, i.e., heat compensation by the shift in the time or space$^1$. Thus, heat storage materials are crucial for realizing the time-/space shift in motor vehicles and solar-thermal electric generation. In particular, as the time-/space shift permits the storage of heat during the day and radiates the heat during the night, its use is also expected for the retention of temperature in a severe area experiencing a large temperature difference, e.g., an extra-terrestrial space or a planet. Particularly, in the candidate places for migration, which are accessible from the earth, i.e., the moon and Mars, the temperature-difference between the day and night is quite large, and the nighttime is extremely cold. This leads us to consider that a huge electricity is needed to keep the temperature adequate for our existence in the dwelling area and space colony. If the stored solar thermal energy is released in the nighttime, a sharp reduction of the electricity is expected. Thus, heat storage material, which has a good productivity and is expandable, are quite attractive.

Latent heat storage is based on the capture or release of energy when a material undergoes a phase change from, for example, solid to liquid or vice versa. Note that heat storage materials based on this phase transition are referred to as phase change materials (PCMs)$^{2-4}$. PCMs can accumulate thermal energy, which exhibits intermittent characteristics, and subsequently generate heat at a constant (phase-transition) temperature related to the latent heat. For example, ice, paraffin, fatty acids, and inorganic hydrates are well-known PCMs that can store thermal energy at low temperatures (<150 °C)$^5$. The heat storage mechanism of these PCMs involves a solid–liquid phase transition; hence, it is imperative to ensure that the PCM inside the container is maintained in the liquid state. Moreover, some hazards are inevitable, i.e., damage to the container because of the large volume change occurring during the phase transition and leaking out of the liquid. In these circumstances, it is of particular interest in developing new candidates for novel heat storage material, e.g., trititanium pentoxide (Ti$_3$O$_5$) based solid–solid phase transition, microencapsulated metal-based PCM, and so on$^2-4$: Vanadium dioxide (VO$_2$) exhibits a strongly correlated electron system, which exhibits a structural phase transition at 68 °C. A reversible change is observed between the monoclinic (low-temperature phase) and tetragonal (high-temperature phase) crystal structures accompanied with an exothermic or endothermic reaction (Fig. 1)$^{11-12}$. Hence, the above-mentioned hazards can be avoided. In addition, the latent heat of VO$_2$ (~237 J/cm$^3$) is comparable to that of the PCMs reported thus far$^{13}$, making it adequate for practical applications. Recently, VO$_2$ powder for PCM has been developed and is commercially-available from the companies; Kojundo chemical laboratory Co., Ltd. (Smartec® HS).
and NIPPON DENKO CO., LTD. However, as VO$_2$ is available as a powder, it is mandatory to use a container if the VO$_2$ powder is used as the PCM. In addition, vanadium is a rare metal; hence, VO$_2$ reagents are expensive. Thus, VO$_2$ exhibits some disadvantages that need to be improved so as to enable large-scale PCM applications.

In this study, a new PCM is proposed, i.e., VO$_2$-dispersed glass, where the VO$_2$ powders embedded in the glass matrix, serves as a durable container-free PCM and prevents the degradation of the VO$_2$ phase because of oxidation and moisture. Glass exhibits immense advantages from the viewpoint of materials science, e.g., large-scale or mass production, flexibility, and formability. Hence, recently, glass has been extensively examined not only for photonics but also as energy-related materials$^{14-17}$. Based on this background, VO$_2$-dispersed glass exhibits immense potential for PCM on the basis of the solid–solid phase transition. An incorporation method$^{18}$ is utilised for fabricating the dispersed glass (Fig. 2), aiming to realise the all-solid PCM.

**Results**

**Selection of the glass matrix composition.** First, several glasses were prepared to investigate the composition of the glass matrix suitable for the VO$_2$ dispersion. In this study, three compositions as candidates for the glass matrix, i.e., 35BaO–65B$_2$O$_3$, 15B$_2$O$_3$–10P$_2$O$_5$–75V$_2$O$_5$, and 30BaO–10TeO$_2$–60V$_2$O$_5$, were examined. A borate system was selected because of a previously reported study in which vanadate compounds have been embedded in a borate glass matrix$^{19}$. Vanadate systems have been selected because a low-processing temperature is expected for synthesis$^{20-22}$.

![Figure 1](image1.png) **Figure 1.** Endothermic or exothermic reaction of the VO$_2$ phase caused by phase transition. DTA measurement was carried out using reagent-grade VO$_2$ powder. In the DTA curves, endothermic and exothermic peaks were observed in the heating and cooling processes, respectively, corresponding to the phase transition between the monoclinic and tetragonal (rutile-type) structures at a $T_c$ of $\sim$68 $^\circ$C.

![Figure 2](image2.png) **Figure 2.** Incorporation method for the preparation of the VO$_2$-dispersed glass. (a) The powdered glass matrix and VO$_2$ powder were mixed, and the mixture was subsequently added into a crucible with a lid. (b) The mixture was melted in an electric furnace. (c) The melts were poured onto a steel plate and were quenched by another steel plate. (d) The VO$_2$-dispersed glass was obtained.
Differential thermal analysis (DTA) (Fig. 3(a)) revealed that the BaO–B₂O₃ and BaO–TeO₂–V₂O₅ systems exhibit high thermal stability against crystallisation because the exothermic peak corresponding to the amorphous–crystal phase transformation was absent, whereas a strong, sharp crystallisation peak was observed for the B₂O₃–P₂O₅–V₂O₅ system, corresponding to formation of the V₂O₅ phase (inset). On the other hand, vanadate systems exhibited a considerably lower glass-transition temperature (T_g) compared with that of the borate system. A low T_g is preferable for the VO₂ dispersion to proceed at a low temperature with respect to energy savings as well as the prevention of degradation of VO₂ because of high-temperature exposure.

Next, the incorporation method was carried out as a trial to fabricate VO₂-dispersed glasses, which were subsequently analysed by powder X-ray diffraction (XRD) (Fig. 3(b)). The VO₂ phase in the borate system was transformed into V₃O₅ (or the so-called Magneli phase) (Fig. S2), and the size of the Magneli phase (~10 μm, Supplementary Fig. S2) is less than that of the VO₂ reagent (~20 μm, Supplementary Fig. S1), suggesting the elution or diffusion of vanadium into the BaO–B₂O₃ glass matrix. On the other hand, the VO₂ phase was stably retained in case of the vanadate systems. This result led us to expect that vanadate systems are suitable for fabricating VO₂-dispersed samples. In addition, the water stability test was carried out using the candidate vanadate system glasses. After the immersion of the B₂O₃–P₂O₅–V₂O₅ system glass into water, a pale-yellow colour was immediately observed, and then the water became black after 1 week (Fig. 3(c)). Meanwhile, the BaO–TeO₂–V₂O₅ system remained transparent, indicative of its high resistivity against water or moisture. Thus, the BaO–TeO₂–V₂O₅ system demonstrates immense potential as glass matrices, which can be used for the VO₂-dispersed PCM. Hence, 30BaO–10TeO₂–60V₂O₅ is selected as the glass matrix.

Characterisation of the VO₂-dispersed glass. VO₂-dispersed glasses with different additive amounts (x; mol%) of VO₂ powder, i.e., 30BaO–10TeO₂–60V₂O₅xVO₂ composites, were fabricated according to the
protocol described in the Method section. Scanning electron microscopy (SEM) analyses revealed that the incorporated VO$_2$ powders are stably embedded in the matrix, with no significant aggregation of the powders ($x = 80$; Fig. 4(a)). Elemental mapping results revealed a clear boundary between the VO$_2$ particles and glass phases. In addition, the migration of barium (Ba) and tellurium (Te) surrounding the VO$_2$ particles and the diffusion of vanadium (V) into the glass matrix were barely observed. To primarily examine the heat storage property, thermal cycling test was also carried out by means of DTA in the VO$_2$-dispersed sample. Clear endothermic and exothermic peaks were observed in the temperature range of ~60–80 °C, which are attributed to the phase-transition of VO$_2$, during the heating and cooling process, respectively. (Fig. 4(b)). The peaks of 10-cycle could be almost superimposed on that of 1-cycle. In addition, the SEM observation revealed no significant change in the microstructure for the sample after the cycling test (Supplementary Fig. S3). Since any collapses were hardly observed in the sample subjected to the cycling test, it is suggested that the dispersed glass possesses a high thermal repeatability.

**Thermal properties.** To examine the latent heat storage function in detail, DSC measurements were carried out. A steep change in the specific heat (peak of the $C_p$–T curve), related to the phase transition of the dispersed VO$_2$ powder, was observed around the phase-transition temperature of VO$_2$ (T$_c$~68 °C), and then the transition enthalpy ($\Delta H$), which corresponded to the latent heat storage capacity, was estimated (Fig. 5a,b, and c) for $x = 60, 80,$ and 120, respectively. The $\Delta H$ values increased with $x$, and finally the sample with $x = 120$ exhibited a $\Delta H$ value of ~14.3 J/g (Fig. 5(d)), corresponding to ca. 30% of that of the VO$_2$ reagent (~45 J/g, Supplementary Fig. S1). Thus, the latent heat storage function is imparted to the glass-based material via the VO$_2$ dispersion. In addition, the temperature retention property of the VO$_2$-dispersed glass was assessed. Small pieces of matrix glass
(free from VO₂, bulk state) and dispersed glass (x = 120, bulk) and VO₂ reagent (powder), with similar weight (~2.2–2.4 g), were heated at around ~100 °C, and then were left at room temperature (RT). Variations in the surface temperature were monitored by thermography. In the matrix glass, the temperature monotonically decreased with time, eventually returning to RT (Fig. 6a). On the other hand, the VO₂ reagent exhibited a temperature plateau for ~2.5 min, corresponding to the latent heat related to the phase transition, with subsequent cooling to RT. In addition, the dispersed glass exhibited a plateau for ~1.5 min, indicative of the temperature retention properties. Thermographic images also aided in the better understanding of the temperature variation. The dispersed glass and VO₂ reagent exhibited similar temperature distribution after ~1 min (start of the plateau) (Fig. 6b). Notably, the VO₂ reagent exhibited a fluctuation in the image colour, indicative of a non-homogeneous temperature gradient. This fluctuation was related to the difference in the packing density of the VO₂ powder. However, the dispersed glass barely exhibited any fluctuation.

Discussion

VO₂ is a glass-forming oxide according to Sun’s classification²⁴, and is easily vitrified by addition of network-modifiers²⁵. VO₂ is the major component in the examined B₂O₃–P₂O₅–V₂O₅ and BaO–TeO₂–V₂O₅ glasses. Although both of these glasses exhibited low Tᵥ, their thermal stabilities against crystallisation and water resistivity were considerably different. A previous study on the glass structure in the P₂O₅–V₂O₅ system have reported that the glass network comprises layers of pyramidal VO₅ units, which are interlinked together by PO₄ units²⁶. Because of the open network structure of glass, water molecules easily attack the PO₄ units²⁷–³⁰, eventually destroying the glass network. Hence, the low stability and resistivity in B₂O₃–P₂O₅–V₂O₅ are thought to be related to a similar structural scenario. Meanwhile, the glasses in the TeO₂–V₂O₅ system comprise of V–O and Te–O polyhedral units, leading to a three-dimensional network structure in binary and multicomponent systems³¹–³³.
Hence, it is hypothesised that a 3D structure provides a stable network and considerably contributes to the high thermal stability against crystallisation and water resistivity in the BaO–TeO2–V2O5 system.

The homogeneity in the temperature retention (no fluctuation of temperature distribution, Fig. 5) was observed in the dispersed glass, and the presence of the glassy phase probably contributed to the minimisation of the pores occurring between the VO2 particles, which necessarily occurred in the powder state. Temperature fluctuations should be enlarged via the expansion of the material in case the PCM powder is used; hence, dispersion or incorporation plays a crucial role in maintaining the homogeneity of the spatial temperature distribution. Moreover, generally, thermal conductivity (\( \Lambda \)) of multicomponent glass possesses \( \Lambda \approx 1 \text{ Wm}^{-1}\text{K}^{-1} \), regardless of its composition/system, and such a low \( \Lambda \) originates in prevention of phonon-propagation due to the random-network (disordered) structure without transition symmetry, e.g., 40P2O5–60V2O5 glass; \( \Lambda \approx 0.8 \text{ Wm}^{-1}\text{K}^{-1} \) (at 350 K or 77 °C)31. Although the \( \Lambda \)-value of matrix glass in this study (30BaO–10TeO2–60V2O5) is considered to be lower than that of VO2 crystal (\( \Lambda \approx 4 \text{ Wm}^{-1}\text{K}^{-1} \) and \( \Lambda \approx 5 \text{ Wm}^{-1}\text{K}^{-1} \) in monoclinic and tetragonal systems, respectively)32, the low \( \Lambda \)-value of glass is possibly preferable from the viewpoint of heat-retaining property because a gradual cooling is expected in the VO2-dispersed glass before/after temperature retention (plateau), and we can also see this trend in Fig. 6(a). The acquisition of the temperature retention properties in glass materials with the dispersion or immobilisation of the VO2 phase is expected to be valuable to exploit new functions and applications.

There are some reports about heat storage material consisting of polymers, e.g., polymer blend PCM. However, taking that oxide (or ceramic) material basically possess a high mechanical/thermal properties compared to polymer (organic) material into account, glass-based PCM is expected to have a long-term reliability. Furthermore, glass-based PCMs are considered to demonstrate potential for massive thermal storage applications, for example, in space development and terraforming, on the basis of the advantages of glass materials, e.g., large-scale and mass production. In particular, the presence of abundant glass and related minerals (e.g., pyroxene and olivine) on Mars33 has also vigorously stimulated the study of glass-based PCMs.

In conclusion, a new PCM based on glass materials, i.e., VO2-dispersed glass in multicomponent systems, is reported, and its latent heat storage and temperature retention properties are demonstrated. On the other hand, because of the dispersed glass still being a prototype, some issues should be overcome, e.g., improvement of the heat storage amount. Nevertheless, as the technology for glass–crystal composites and their industrialisation has been previously reported34, the results obtained herein demonstrate significance as the first step in the development of all-solid PCMs.
Methods
Preparation of the matrix glass. The glass matrix compositions were 35BaO–65B₂O₃, 15BaO–10P₂O₅–75V₂O₅, and 30BaO–10TeO₂–60V₂O₅ (mol%). Commercial reagent-grade powders of BaCO₃, B₂O₃, (NH₄)₂HPO₄, V₂O₅, and TeO₂ were used as raw materials. Glasses were prepared by a conventional melt-quenching technique using an alumina crucible with a lid. Melting conditions were as follows: 1200°C for 30 min (BaO–B₂O₃ system), 800°C for 60 min (B₂O₃–P₂O₅–V₂O₅), and 800°C for 60 min (BaO–TeO₂–V₂O₅) under air. The melts were poured onto a steel plate heated at ~200°C, followed by pressing using another steel plate to obtain the as-quenched samples (Quenching rate: ~10⁻¹–10² K/sec). Their samples were confirmed to be in the glassy state as evidenced by X-ray diffraction (XRD) analysis.

Dispersion of VO₂ in the glass matrix. To fabricate the VO₂-dispersed glass, the incorporation method reported in the study by Komatsu et al. was utilised. Figure 2 shows the schematics of the procedure. A powdered matrix glass and VO₂ powder (purity: 99.9%; Kojundo Chemical Laboratory Co., Ltd.) were thoroughly mixed using an alumina mortar. Second, the mixture was added into an alumina crucible and melted under the following conditions: 1200°C for 10 min (BaO–B₂O₃ system), 1200°C for 15 min (B₂O₃–P₂O₅–V₂O₅), and 900°C for 10 min (BaO–TeO₂–V₂O₅) under air. The quenching process was similar to that utilised during the preparation of the matrix glass, finally furnishing VO₂-dispersed glasses with different matrices.

Characterisation of the matrix glass and VO₂-dispersed glass. In the studied glasses and VO₂-dispersed samples, the state of the material and crystals were observed by XRD (Cu-Kα radiation). Microscopic observation was carried out by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy. Water stability was examined by the immersion of the samples (~0.2 g; bulk form) into water.

The thermal properties of the matrix and VO₂-dispersed glasses were examined by differential thermal analysis (DTA; heating rate of 10 K/min, Rigaku Corporation, Thermoplus TG8120). The transition enthalpy (ΔH), corresponding to the amount of the stored latent heat, of the VO₂-dispersed samples was evaluated by differential scanning calorimetry (DSC; heating rate of 1 K/min, Seiko Instruments Inc., DSC6220). The specific heat Cᵥ [J/(mol·K)] was measured as a function of temperature (T), and ΔH was estimated on the basis of the thermodynamic relation: ΔH = ∫CᵥdT. The sample state used in the measurement was the bulk form with a weight of ca. 10 mg. The time dependence of temperature in the examined samples was evaluated by a thermography test (Nippon Avionics Co., Ltd.; R300SR-S).

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Author Contributions
K.M. fabricated and characterised the materials. Y.T., N.T. and T.F. designed the study; Y.Y. and S.S. contributed to the thermal analysis; and Y.T. and T.F. wrote the paper.

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