Preparation of Hydrothermally Solidified Materials from Waste Cathode Ray Tube Panel Glass for Construction Applications

Qingbo Xu
Solid Waste Management Center of Sanmenxia Ecological Environment Protection Bureau
Jing Zhang
Zhengzhou University
Shunyi Li (lsy76@163.com)
Zhengzhou University https://orcid.org/0000-0001-7570-5572

Research Article

Keywords: CRT panel glass, Hydrothermal solidification processing, Waste recycling, Tobermorite, construction material, Flexural strength

Posted Date: March 22nd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-212314/v1

Abstract

Solidification of cathode ray tube (CRT) panel glass was carried out using a hydrothermal processing method. In this way, the glass powder was first compacted in a mold at 20 MPa, and then hydrothermally cured in an autoclave under saturated steam pressure at 200 ℃ for 6 hours. The CRT panel glass was then hydrothermally solidified by the formation of tobermorite ($Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$), which was encouraged by the addition of slaked lime ($Ca(OH)_2$). The final solidified specimen's strength was heavily depended on the amount of tobermorite formed, with higher concentrations of tobermorite producing commensurately greater mechanical strength. With the addition of slaked lime at 20%-30% by mass, the specimen achieved a flexural strength of approximately 16 MPa, which is sufficiently great for using as a construction material. As such, there is cause to believe that the hydrothermal processing method used here may have substantial potential for the product of high-quality recycled CRT panel glass with properties suitable for utilization as a construction material.

1. Introduction

The rapid transition towards more energy-efficient displays has made cathode ray tube (CRT) glass largely obsolete and produced a major disposal problem of global concern. By 2016, 44.7 million metric tonnes (Mt) of e-waste was generated globally. However, only 20% of it was recycled through appropriate channels (Baldé CP et al. 2017). The CRTs account for a significant portion of the e-waste stream. According to the United Nations University, the quantity of CRT screen waste generated globally in 2014 was approximately 6.3 Mt (Balde CP et al. 2015). In 2014, Asia generated the most of the screen waste among all continents (2.5 Mt) , followed by Europe (1.7 Mt), America (1.7 Mt), Africa (0.3 Mt) and Oceania (0.1 Mt) (Singh N et al. 2016). Globally, it is estimated that only ~25% of the discarded CRTs are recycled, ~60% are landfilled and ~15% are incinerated (Domingos T 2008). Generally, closed-loop recycling (using the scrap glass to manufacture more new CRT glass) is the most prevalent method used to manage CRT glass waste, but this may be impractical going forward due to the shrinking global market for CRT products (Xu QB et al. 2012). The second way to recycle CRT glass waste is to reuse it as an input in another production cycle—i.e., to replace sand as a flux in smelting and brick manufacturing industries (Dondi M et al. 2009; Loryuenyong V et al. 2009), foam glass production(Bernardo E and Albertini F 2006; Guo HW et al. 2010; Konig J et al. 2015), ceramic glazes (Andreola F et al. 2007), glass containers, table-ware or glass fibers (Pozzi P et al. 2010).The use of CRT glass as a secondary raw material, however, is strictly limited by the demand for and quality of the usable material produced from it. Additionally, this manner of recycling CRT glass is not extensively utilized due to its low profitability, largely a result of the high cost of processing it to meet manufacturers' standards (Ravi V 2012). Furthermore, common disposal practices such as glass smelting or discarding of electronics in landfills are becoming obsolete and unsustainable due to the associated environmental risks (Xu QB et al. 2013). Therefore, more low-cost and environmentally friendly recycling methods need to be developed to solve the current issues with CRT glass waste management.

Hydrothermal processes, simulating the formation of sedimentary rock sequences, are useful for the synthesis and solidification of materials with low hydrothermal autoclaving temperatures (below 300 °C) (Yamasaki N 2003). Hydrothermal processes are proposed as a potential approach in the development of a new sustainable system loop for recycling the byproducts or solid wastes. In recent years, A hydrothermal processing technique has been applied to the solidification of inorganic wastes. Such as the metal-contaminated soil, solidification of municipal solid waste incineration bottom ash (Jing ZZ et al. 2013; Jing ZZ et al. 2016) and river sediment (Jing ZZ et al. 2009).This technical method has been also applied to convert concrete waste into new construction materials. Relevant solidification behavior of a $CaO–SiO_2–H_2O$ system has been studied by a hydrothermal process (Sarkar R et al. 2006; Yamasaki N et al. 1990). The deposits formed in the particles of the starting materials have been shown to enhance the material strength. During the treatment in a $CaO–SiO_2–H_2O$ system, the material strength of hydrothermal solidified product was improved (Maeda H et al. 2007). Furthermore, researchers have reported that hydrothermal reactions is of great importance in the immobilization of heavy metals (Inoue R and Suito H 2002; Tae SJ et al. 2017). As CRT panel glass has a similar chemical composition to the above inorganic wastes. Under hydrothermal conditions, it may form well crystallized hydrated calcium silicates. In the meanwhile, it may also form strong networks with superior mechanical properties. Therefore, this hydrothermal technology has great potential to assist in utilizing waste on a massive scale by lowering energy consumption requirements due to the lower temperature necessitated by hydrothermal autoclaving as compared to currently wide-spread waste processing techniques. As far as we know, there appears to be no published work dealing with the use of hydrothermal solidification techniques on cathode ray tube (CRT) panel glass.

This study used CRT panel glass as a raw material for hydrothermal solidification. The objective of the research is to experimentally investigate the influences of additives, autoclave temperature, and time on the mechanical properties of solidified bodies. It is expected that the results will provide practical information that should prove invaluable for the development of new uses of the material—e.g., as indoor laying material (tiles and blocks) and other similar-scale construction applications.

2. Experimental Procedure

The raw material used for hydrothermal processing in this study was CRT panel glass. The CRT panel glass was collected from an e-waste recycling plant named TES-AMM in Shanghai. The panel glass' fluorescent coating was removed by manual abrasion, and then dried the glass at 110°C. The cullet glass was then crushed, and dry-milled using a ball mill (QM-3SP2, Nanjing) at 580 rpm for 30 min, and then was sieved through a mesh of 74 μm. The chemical composition of the panel glass, determined by X-ray fluorescence (XRF, Philips PW 2404), is shown in **Table 1**. A mixture of the panel glass powder and slaked lime (calcium hydroxide) additive was added to 5 mass percent of distilled water; then the mixture was compacted by uniaxial pressing in a stainless-steel die (Ø40 mm, H30 mm). The composition of slaked lime was varied from 10 to 40 mass percent. Under the condition of compaction pressure range of 10-40 MPa, the demolded specimens were set in a Teflon-lined stainless-steel apparatus (volume: 250 cm^3) and

subjected to hydrothermal treatment under saturated steam pressure at 50-200 °C for 2-12 h. The hydrothermal apparatus used for curing the demolded specimens is shown in **Fig 1**. The mechanical and chemical properties of the cured specimens were tested.

Table 1 Chemical composition in oxide % of CRT panel glass determined by X-ray fluorescence

Mass (%)	SiO_2	Al_2O_3	CaO	PbO	Na_2O	K_2O	BaO	SrO
Panel	58.4	2.07	0.21	_	8.63	8.32	8.69	7.63

The solidified disc-shaped specimens were cut into rectangular-shaped samples of 80×10×6 mm, and then were used to determine the three point flexural strength of the finished material. The measurements were conducted in triplicate by a strength testing machine (XO-106A, Xie Qiang Instrument Technology) at a loading rate of 0.5 mm/min.The strength values are averages of the measurements. Flexural strength is the measurement used because we envision that these hydrothermal products will find primary use as indoor laying material (e.g. tiles). The flexural bend strength (FBS) was calculated using the following equation:

$$\delta = \frac{3FL}{2bd^2} \cdots$$

where: F is the load (force) at the fracture point (N);

L is the length of the support span (mm);

b is width (mm); d is thickness (mm)

After the strength testing, the microstructure of the solidified specimens was observed with a scanning electron microscope (SEM; S-4800). X-ray diffraction analyses (XRD, D8 Advance) were carried out to investigate the morphologies of the hydrates.

3. Results And Dicussion

3.1 Effect of slaked lime addition

The addition of slaked lime was expected to increase the strength of the solidified bodies. Consequently, the effect of the slaked lime content was investigated first. **Fig. 2** shows the effect of the slaked lime content on the flexural strength of the solidified specimen. With increasing slaked lime content up to 20 mass percent, the flexural strength increases rapidly, and then appears to decrease slightly for larger slaked lime contents. The flexural strength reaches 16 MPa for the slaked lime content of 20 mass percent in the solidified specimens, approximately 1.6 times that of the specimens prepared with 10 mass

percent slaked lime. This is a great enough strength for use as a construction material. The strength enhancement is due to the fact that the addition of slaked lime causes formation of tobermorite in the material. When the content of slaked lime is 20 mass percent and 30 mass percent, the Ca/Si molar ratio is approximately 0.35 and 0.61, respectively, this is in disagreement with previous studies indicating that the Ca/Si of starting materials should fall near the stoichiometric Ca/Si ratio for tobermorite (0.83) (Etoh J et al. 2009; Naganathan S et al. 2010). The possible reason for this is that in the CRT panel glass, the network is very condensed, and only a little silicon can be dissolved from the network in hydrothermal conditions.

The phase evolution of the above samples with different content of hydrated lime was studied by XRD analysis (**Fig. 3)**. With the addition of slaked lime, a new phase corresponding to 1.1 nm tobermorite ($Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$) formed. When the slaked lime content was 20 mass percent, the intensity of tobermorite peaks tended to be strongest. And the flexural strength was obviously enhanced. The above results indicate that there is a most suitable content of slaked lime for tobermorite formation. With the increase of slaked lime content up to 40 percent, the intensity of tobermorite formation tended to decrease, indicating that too much slaked lime has a negative effect on the strength of the solidified specimen.

The main reason may be that the unreacted slaked lime and the new Portlandite ($Ca(OH)_2$) forms a protective film in the surface of the reaction core, and prevents further hydrothermal reaction. The same results were obtained for the hydrothermal solidification of coal fly ash (Jing Z et al. 2006). It was pointed out that $Ca(OH)_2$ retards the hydration of cement compounds by forming a protective coating on the surface of un-hydrated compounds.

Fig. 4 shows SEM photographs of the fracture surface of the specimen synthesized with 10 mass percent and 20 mass percent slaked lime. Both were cured at 200°C for 6 h. Fibrous tobermorite forms, and the needle-like tobermorite bonds formed silt particles together and fills in the spaces between these particles, thus reinforcing the strength of solidified specimens (**Fig. 4 (b)**); while little tobermorite can be found for the specimen with 10 mass percent slaked lime added (**Fig. 4 (a)**). From these SEM photographs it can be seen that the tobermorite formed looks like fiber reinforcement , resulting in an enhancement of flexural strength in the solidified bodies.

3.2 Compaction pressure

In the hydrothermal processing mentioned previously, the raw material was first compacted, then cured in the autoclave. It is expected that the compaction pressure will affect the mechanical properties of the solidified bodies. **Fig. 5** shows the relationships between the compaction pressure, apparent density, and

flexural strength of the solidified bodies. It can be seen that the flexural strength and apparent density increase with the increase of compaction pressure. The density of solidified bodies reflects the degree of contact between particles. Close contact between particles may accelerate the hydrothermal reaction, thereby improving the strength of the solidified body. Furthermore, fine deposits formed on the surface of glass aggregates under the higher pressure conditions filled the spaces between particles of the starting materials, leading to the increase of the strength (Maeda H et al. 2009). It is worth noting that the apparent density increases when the compaction pressure exceeds 10 MPa, and the flexural strength increases rapidly until the maximum flexural strength of 22 MPa is reached at the compaction pressure of 30 MPa. However, the flexural strength begins to decrease rapidly when the pressure reaches and then exceeds 40 MPa. This occurs because under the conditions of such high pressures, the mold body easily generates cracks, and these cracks result in negative effects on body strength.

3.3 Autoclave curing time and temperature

The effects of autoclave curing temperature and time on the flexural strength of the solidified bodies are shown in **Figs. 6 and 7**. In addition, the processing conditions were identical to the reference conditions. In **Fig. 6**, it is clearly illustrated that increases in autoclave temperature lead to the increase of the flexural strength of the solidified bodies. For instance, the flexural strength of the specimens at 200 °C is about 4 times of that at 50 °C , suggesting that there is a linear relationship between the flexural strength and the curing temperature. After hydrothermal processing at 200 ℃, it is speculated that a new phase of 1.1nm-tobermorite was formed. As seen in **Fig. 4 (b)**, the same mineral formed bonded glass and $Ca(OH)_2$ particles together, filled the space between glass particles.

4. Conclusions

In this paper, a hydrothermal processing technique is developed. The experimental results for solidification of waste CRT panel glass with this technique can be summarized as follows:

1. The hydrothermal processing was carried out at 50-200 °C for 6-12 h. The flexural strengths of the solidified bodies corresponding to this range of experimental conditions were 3.7-22.5 Mpa.
2. The addition of slaked lime to the panel glass powders was effective in increasing the strength of solidified bodies. It is speculated that the dissolution rate of silica in higher pH solution is enhanced, which accelerates the hydrothermal reaction.
3. It is speculated that the tobermorite formed is the most important constituent that produces strength in the solidified bodies.
4. When the curing time is more than 9 h, due possibly to the disappearance or reduction of tobermorit, the strength of the solidified bodies decreased.

5. In summary, this hydrothermal processing method have a high potential for abetting efforts to reuse/recycle CRT panel glass on a large scale.

Declarations

Acknowledgements

This study was supported by the Promotion of Science the Key Research Project of Shanghai in China (Grant no. 10dz1205200) and the National Key Technology R&D Program of China (Grant no. 2008BAC46B02). The authors thank Julie M. Schoenung for checking the quality of the English that improved the clarity of the manuscript.

1. Ethics approval and consent to participate: Not applicable.
2. Consent for publication: Not applicable.
3. Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

4. Competing interests

The authors declare that they have no competing interests.

5. Funding

This study was supported by the Promotion of Science the Key Research Project of Shanghai in China (Grant no. 10dz1205200) and the National Key Technology R&D Program of China (Grant no. 2008BAC46B02).

6. Acknowledgements

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7. Authors' contributions

QX provided ideas, conducted experiments and wrote part of the paper; JZ conducted experiments and wrote part of the paper; SL directed the experiments and the writing of paper and served as corresponding author. All authors read and approved the final manuscript.

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Figures

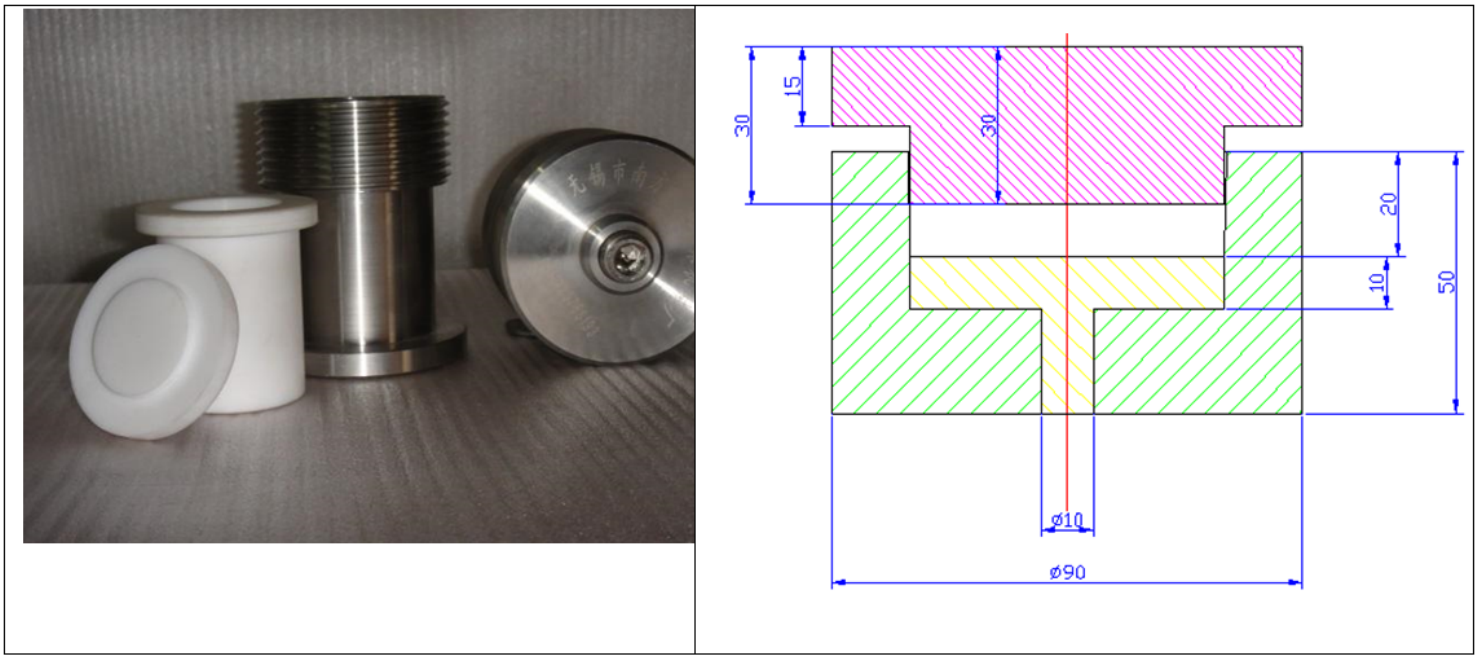

Figure 1

Hydrothermal apparatus used for curing compacted specimens.

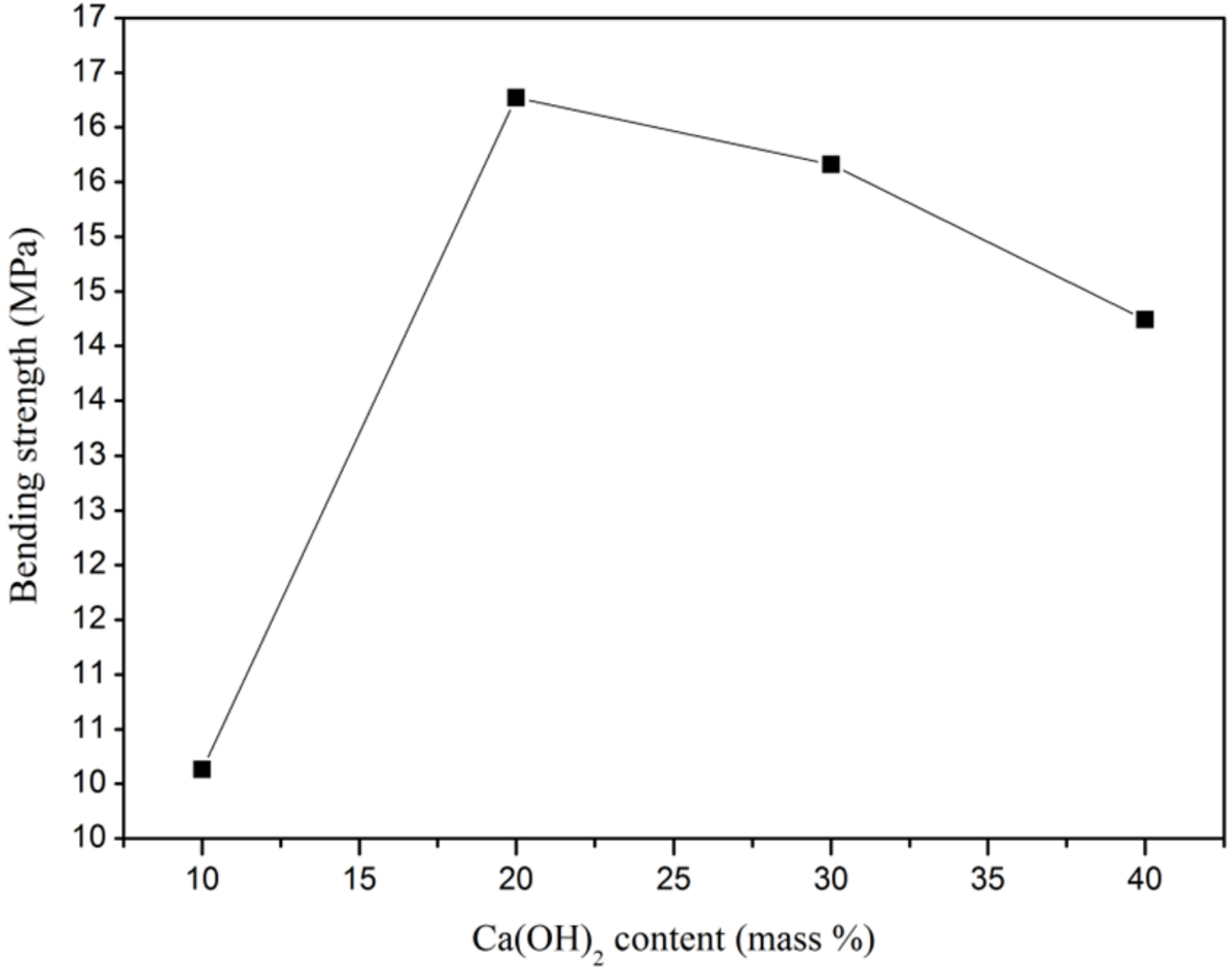

Figure 2

Effect of slaked lime content (mass %) on the bending strength of solidified bodies. Hydrothermal processing conditions: compaction pressure—20 MPa; curing temperature—200°C; Curing time—6 h.

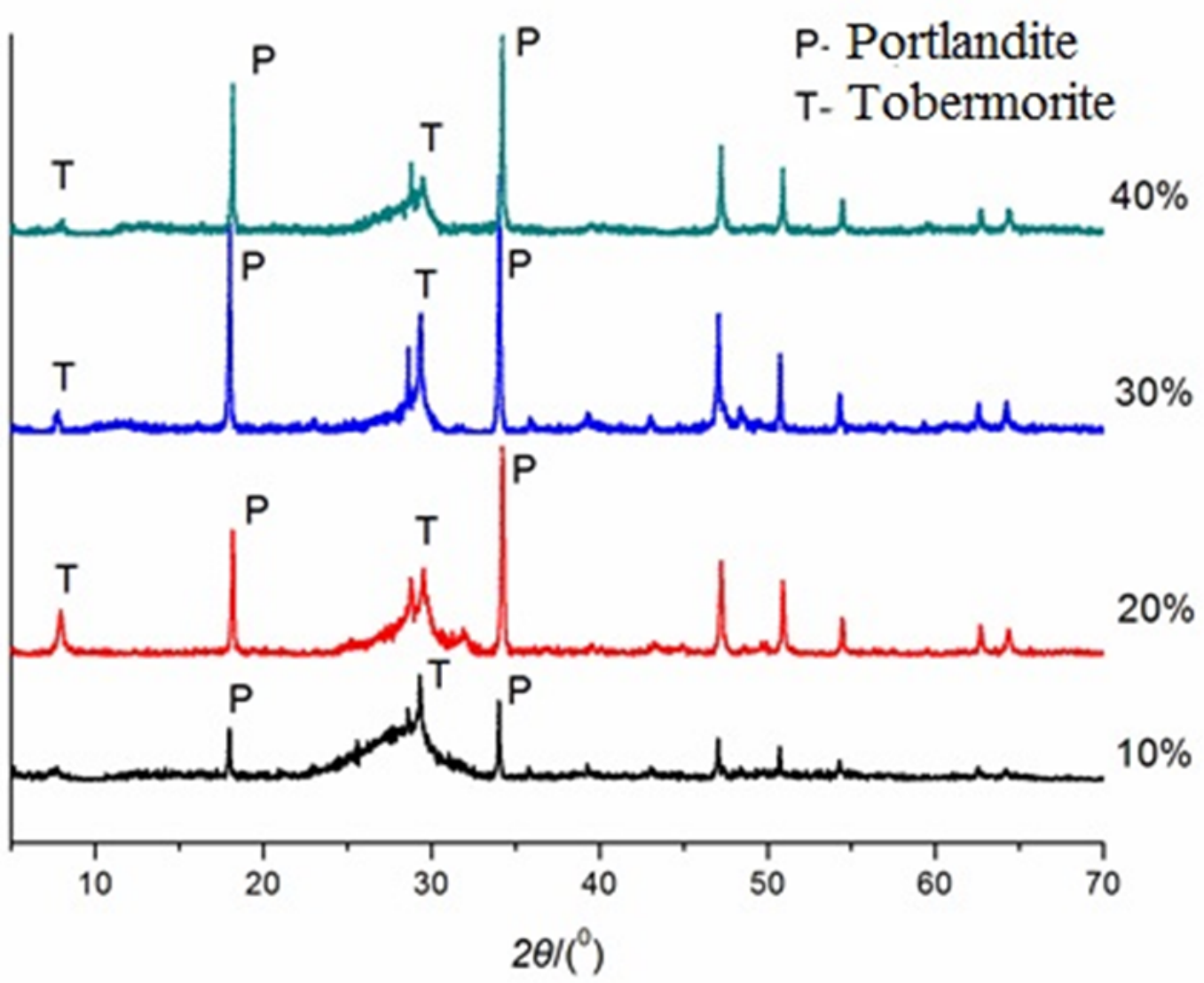

Figure 3

XRD profiles of CRT panel glass with different slaked lime content hydrothermally treated at 200°C for 6 hours.

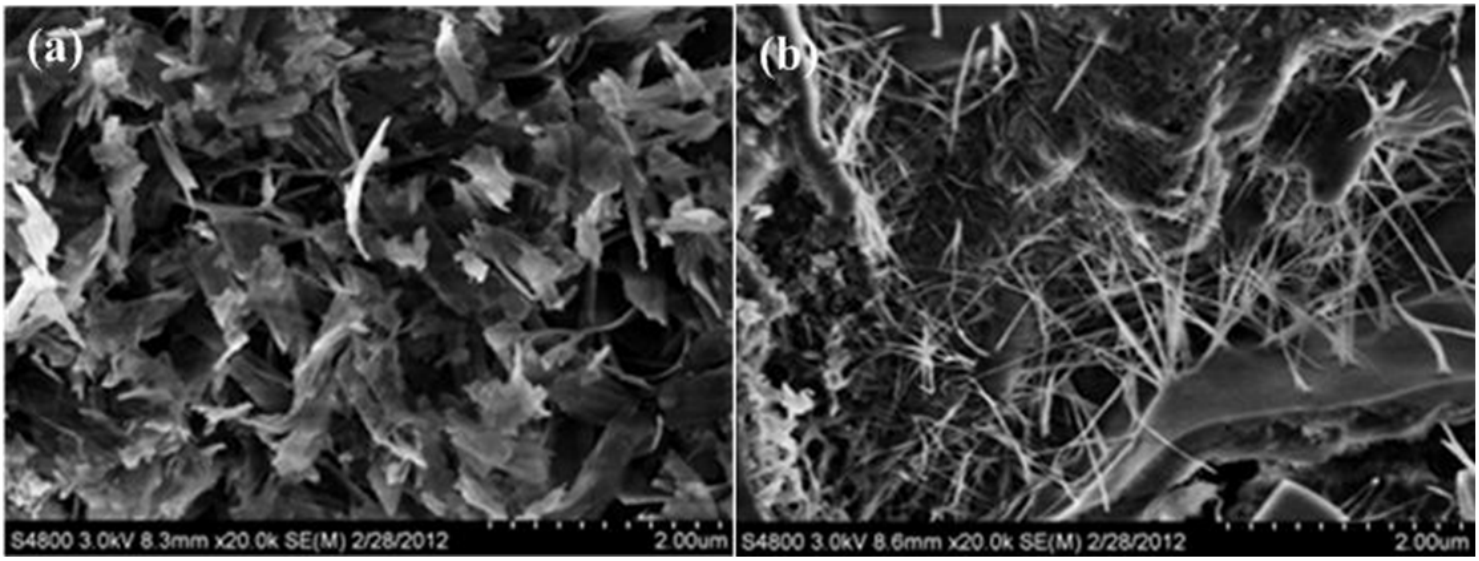

Figure 4

SEM photographs of solidified bodies produced at curing temperature of 200°C, for 6 h. (a)10% slaked lime content; (b) 20% slaked lime content

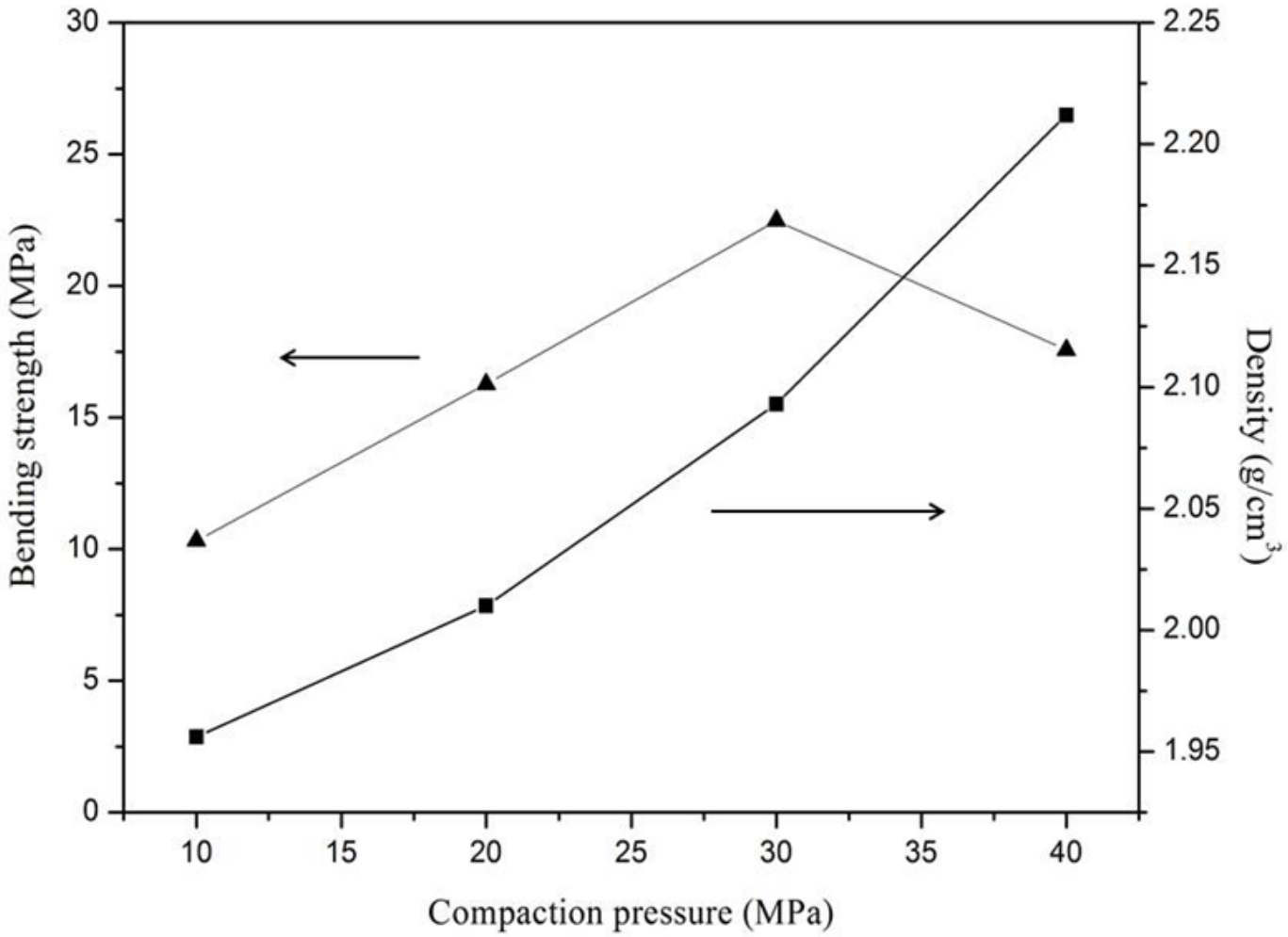

Figure 5

Relationship between the compaction pressure, bending strength and apparent density. Hydrothermal processing conditions: slaked lime content—20 mass%; curing temperature—200 °C; curing time—6 h.

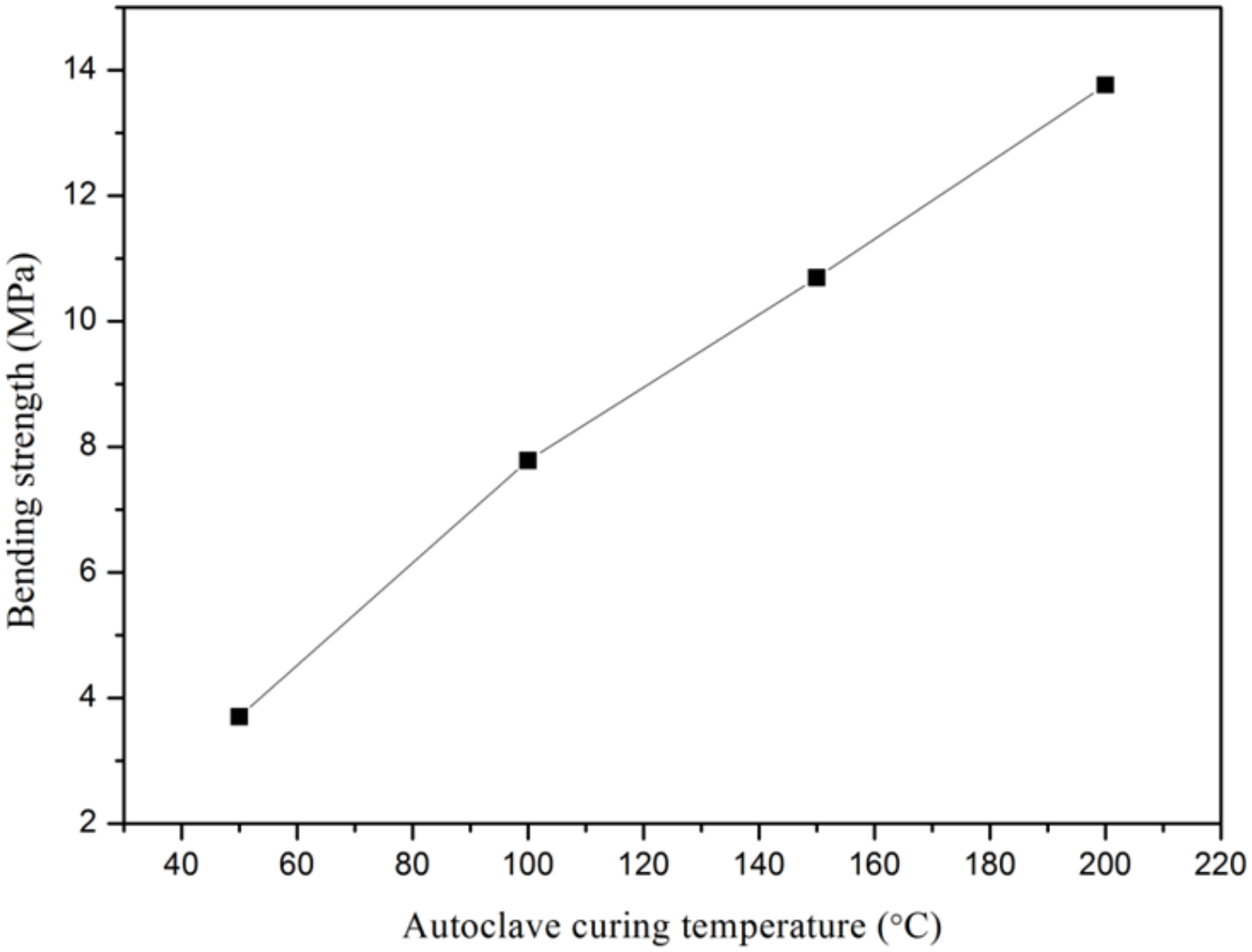

Figure 6

Effect of autoclave curing temperature on the bending strength of solidified bodies. Hydrothermal processing conditions: compaction pressure—20 MPa; hydrated lime content—20 mass%; curing time—6 h.

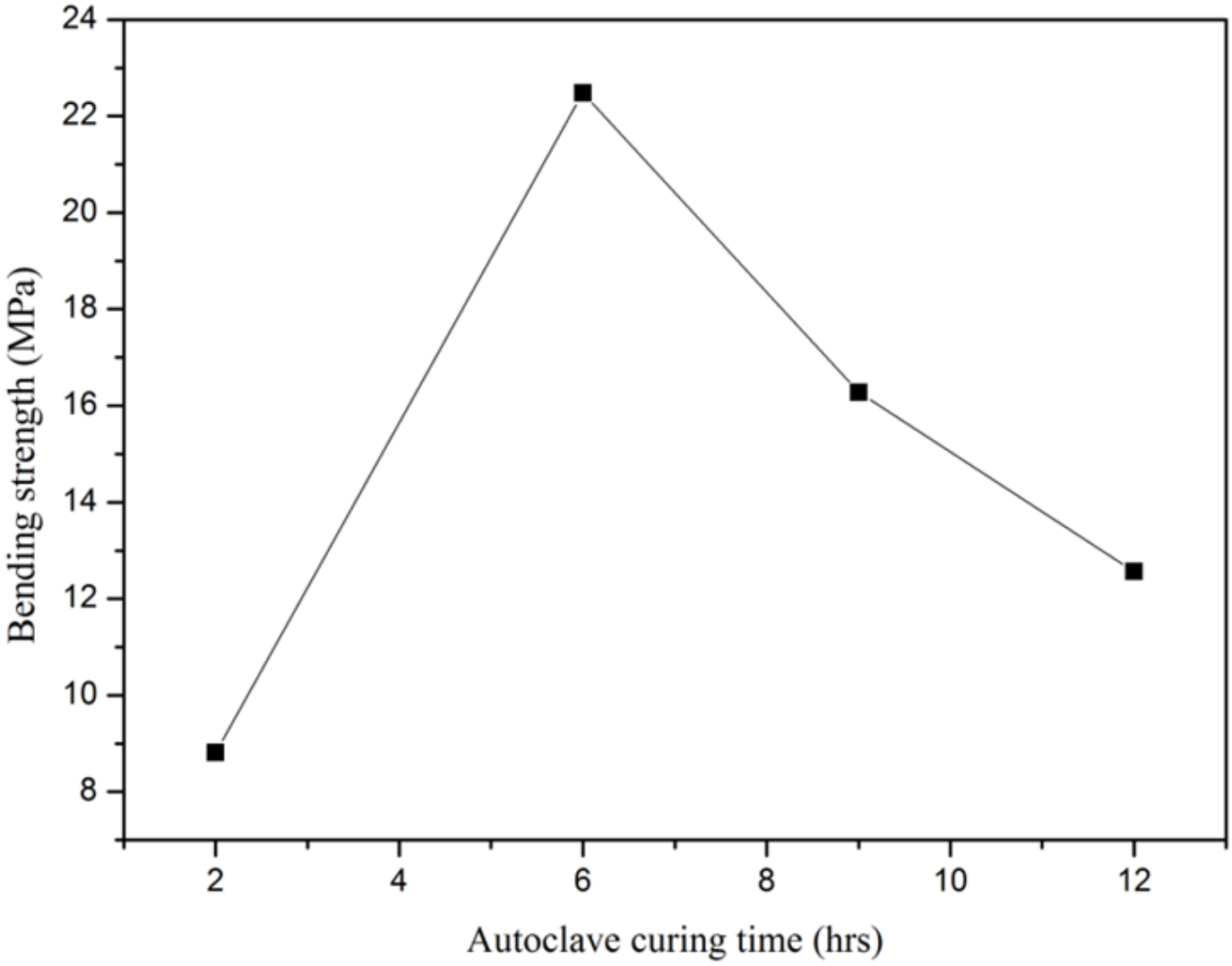

Figure 7

Effect of autoclave curing time on the bending strength of solidified bodies. Hydrothermal processing conditions: compaction pressure—30 MPa; hydrated lime content—20 mass%; curing temperature—200°C.

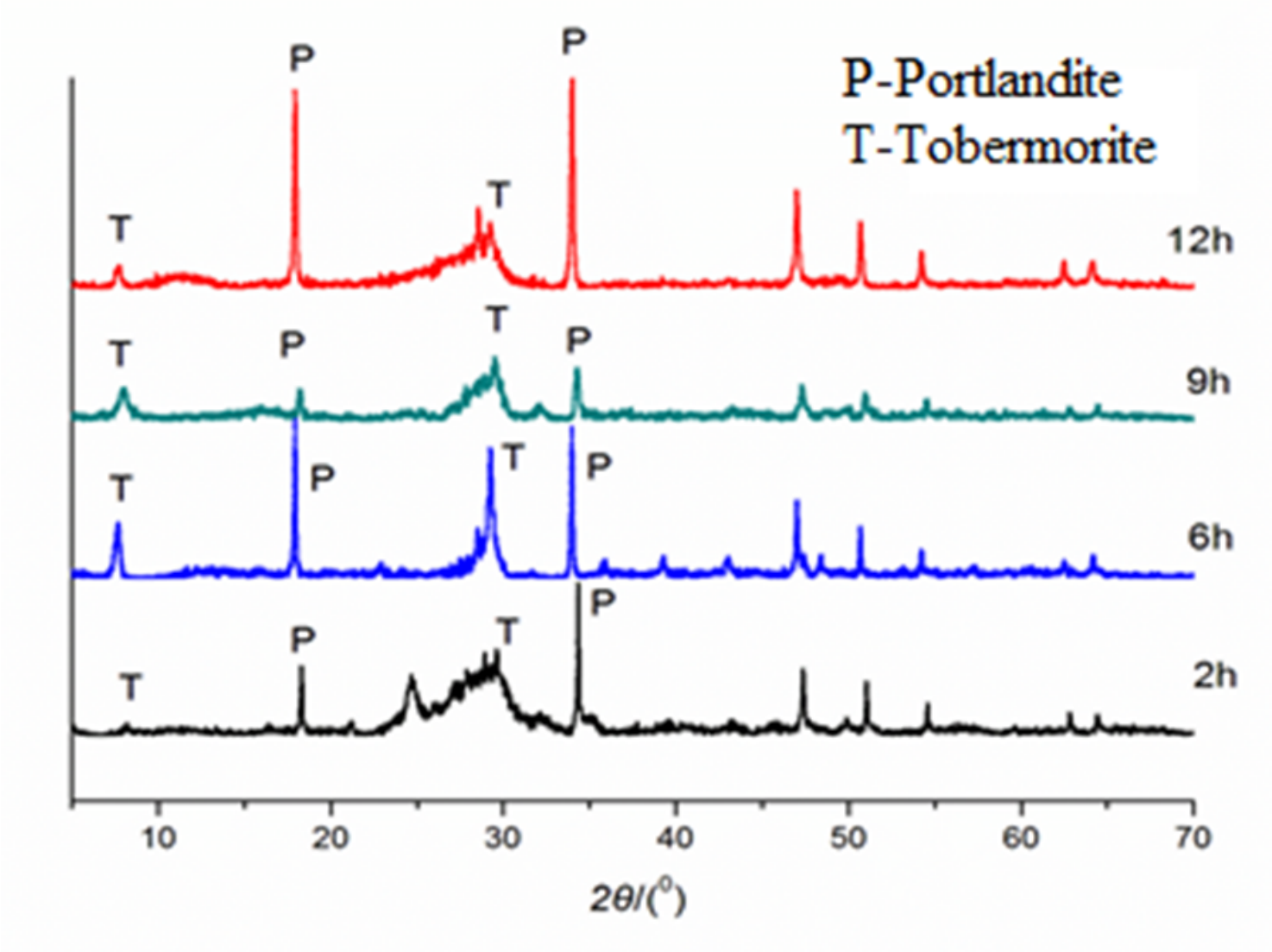

Figure 8

XRD profiles of CRT panel glass hydrothermally solidified bodies with different autoclave curing time treated at 200°Cfor 30 MPa; hydrated lime content—20 mass%;