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Effects of EG:CA Ratios on the Luminescence of BeO Ceramics by Sol-Gel Technique

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This study aims to investigate the effect of ethylene glycol (EG) and citric acid (CA), EG:CA, ratios on the structural, morphological and luminescence properties of BeO ceramics synthesized by sol-gel method. Structural and morphological characterization was done by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analyses, while Luminescence signals were characterized by Radioluminescence (RL), Thermoluminescence (TL) and Optical Stimulated Luminescence (OSL) techniques. XRD diffraction patterns showed that sol-gel synthesis was successful in the production of BeO ceramics and EG:CA ratios significantly changed the BeO structure. While the RL spectra of BeO ceramics synthesized by sol-gel method exhibited very sensitive emission peaks between 200 nm and 500 nm, characteristic of BeO, notable differences were observed in the dominant emission bands. Moreover, it has been proven that TL and OSL signals of samples synthesized using appropriate conditions can be enhanced for dosimetric purposes.

1. Introduction

While oxide-based ceramic materials are generally produced by solid-state reactions of powders and the processing of granular agglomerates at high temperatures, glasses are obtained by melting [1-3]. Recent research and development activities emphasize the importance of chemical synthesis methods using organic precursors in processing and producing ceramics [1]. The sol-gel method is widely used in various applications, such as the mass production of ceramics on a commercial scale. This synthesis method creates reactions at relatively low temperatures, forming powders and producing compounds that cannot be obtained with the solid-state technique [4].

Although the sol-gel process is widely used for powder synthesis, a significant drawback of this method is that the gel-like precursors directly impact particle sizes during synthesis, and these ultrafine particles are subject to severe aggregation during drying [5, 6]. This aggregation can lead to batch reproducibility problems, and improper applications of ethylene glycol (EG) and citric acid (CA), EG:CA, ratios can alter the structural, morphological, and luminescence properties of the final product. It is reported in the literature that EG:CA ratios significantly affect the phase

formation, surface morphology and various physical properties of ceramic materials [7].

TL (Thermoluminescence) and OSL (Optically Stimulated Luminescence) techniques are passive luminescence methods used to measure the dose following the absorption of ionizing radiation by insulating and semiconductor materials [8, 9]. The dose information is obtained through structural defects (traps) within the lattice. The TL method involves thermal stimulation, while the OSL method uses light stimulation. When developing luminescent materials, certain properties are desired, such as high radiation sensitivity, photosensitive trapped charges, dose linearity, and minimal fading (such as mechanical stress and moisture) [10]. Additionally, factors such as exhibiting soft tissue equivalence in terms of effective atomic number (Z_{eff}), minimum dimensions, and cost-effectiveness may play important roles in the viability of the commercial product. While a variety of materials (such as Al_2O_3, BeO, and MgO) have been examined for TL/OSL dosimetry purposes [11-15], the limited proliferation of commercialized dosimetric systems remains a significant challenge.

BeO is an insulator with a wide bandgap of approximately 10.6 eV and has been widely used

commercially in industrial applications since the 1950s [16]. In addition to the material's superior structural, chemical and physical properties, its tissue equivalence (Z_{eff} = 7.13) has made BeO a preferred material in dosimetric applications [17-19]. TL and OSL properties of BeO ceramics have been previously studied in detail for dosimetric applications. Although the material was initially proposed for TL dosimetry, the sensitivity of luminescence signals to light suggested that the material could be a potential candidate for OSL dosimetry, and detailed research was conducted in this direction [19, 20]. The material has been studied in detail in many studies in luminescence applications as synthesized samples or as Thermalox® 995 (Materion Co.) BeO chips, which are widely used in the electronics industry [19-22]. The OSL dosimetry system based on Thermalox chips was developed as a result of successive studies on this material [23-26]. However, BeO Thermalox 995 chips are not materials developed specifically for dosimetric purposes, and many impurity elements such as Si, Mg, Fe, Al, B and Ca are deliberately added to their structure during industrial production stages [27]. Such impurity elements make it difficult to understand and control the luminescence properties of BeO and pose some difficulties regarding the unknown of the luminescence source. For this reason, synthesis processes in different methods are of great importance in terms of OSL dosimetry to better understand and control the luminescence properties of BeO ceramics.

In this study, pure BeO nanoparticles were synthesized with different EG:CA ratios using sol-gel method. To obtain nanostructured ceramics as a promising OSL dosimeter with more homogeneity and high luminescence efficiency, the roles of different gelation agents on phase formation, morphology, grain growth behaviour and luminescence properties were examined. In this study, TL glow curves and OSL decay curves were examined and discussed in detail.

2. Results and Discussion

Figure 1. shows the XRD patterns obtained from BeO ceramics produced with ethylene glycol and citric acid used as gelling agents in different amounts during the sol-gel synthesis process. As can be seen from the figure, the intensities of the XRD peaks increase with the increasing EG:CA ratio and the maximum intensity was obtained at the ratio of 7:1. This clearly shows the effect of changing EG:CA ratio during synthesis on the crystallinity of BeO. The best crystallinity, high XRD peak intensities, low FWHM and defect were obtained at the ratio of 7:1 of EG:CA with low strain. On the

other hand, the broad low-intensity halo peak between 20 and 40 degrees is an indication that the structure still contains amorphous in the 1:1 ratio. With the increasing proportion of ethylene glycol in the structure, strong Be-O bonds tend towards uniform crystallinity. The XRD peaks in all samples matched well with the reference ICDD pdf card number 01-078-1562, which represents the hexagonal pure BeO phase. Average crystallinity sizes, micro strain and dislocation density values were obtained for each sample and are presented in Table 1. Considering the structural parameters presented in the Table, as the EG:CA ratio increases, an increase in the crystallinity of BeO and, accordingly, a lower stress and defect concentration was achieved. It should be noted that the best crystal structure was obtained when EG:CA was 7:1.
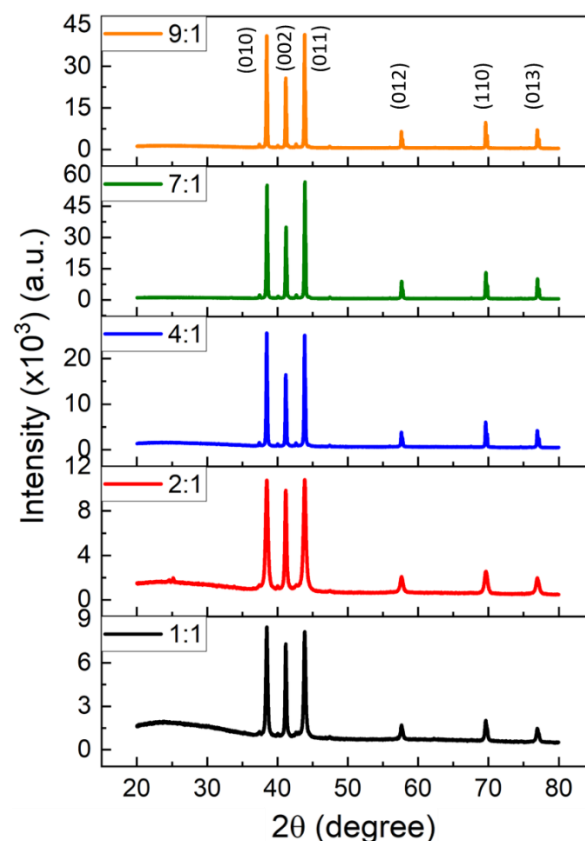

Figure 1. XRD patterns of BeO powders produced by different EG:CA ratios in sol-gel synthesis.

The effect of different EG:CA ratios on the surface morphology of BeO was also examined. Figure 2. shows SEM images of sintered BeO powders produced with EG:CA ratios of 1:1, 2:1, 4:1, 7:1, and 9:1. As can be seen from the figure, it can be said that as the EG ratio increases, the structure offers more regularly placed grains and has a narrow size distribution. 7:1 EG:CA ratio can be recommended for luminescence analyses as the surface is more homogeneous and non-porous.

Table 1. Structural parameter of BeO sintered powder samples by sol-gel synthesis with different EG:CA ratios.

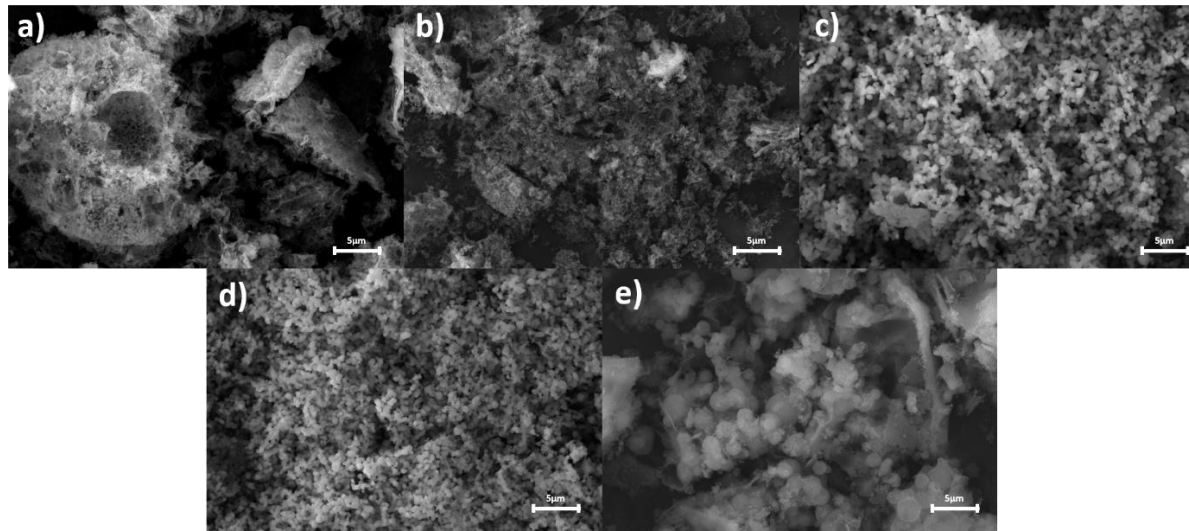| Samples	FWHM, β (°)	Crystallite size, D (nm)	Micro strain, ε x 10^{-2}	Dislocation density, δ (10^{20})
1:1	0.42	21.58	9.48	4.71
2:1	0.31	29.35	7.14	3.33
4:1	0.20	44.58	4.87	2.21
7:1	0.14	70.13	2.93	1.41
9:1	0.19	49.81	4.07	2.07

Figure 2. SEM images of BeO powders produced by different EG:CA ratios in sol-gel synthesis.

Before TL and OSL measurements, RL is a good starting method to see more closely the changes in the luminescence band structure of samples synthesized with different synthesis processes, that is, samples synthesized with different EG:CA ratios. For these reasons, the RL emissions of the samples were collected in the range of 200 nm to 1000 nm and are presented in Figure 3. As can be seen from the figure, all samples are represented by a combined broad sensitive luminescence band located in the range of 200 to 400 nm. The first luminescence band located at 260 nm is the well-known characteristic emission band originating from the self-trapped excitons of BeO [28-30]. On the other hand, a second luminescence band located around 310 nm was also observed in previous studies [31]. Here, changing the EG:CA ratio caused a significant increase in RL signals by activating the characteristic luminescent band with the effect of increasing crystallinity. Although it is observed that BeO's luminescence band shifts towards the end of the UV region with a ratio of 9:1, it can be said that a remarkable decrease is observed in the charge carrier concentration that causes luminescence. The shift in BeO's luminescence band towards the end of the UV region observed with the 9:1 EG:CA ratio can be explained by the formation of additional defects,

such as oxygen vacancies, in the BeO lattice. These defects introduce localized energy levels that influence the emission characteristics. Furthermore, the high concentration of ethylene glycol likely impacts the crystallinity and particle size, which can also contribute to the modification of the material's optical properties. Such structural changes may be responsible for the observed shift in the luminescence spectrum.
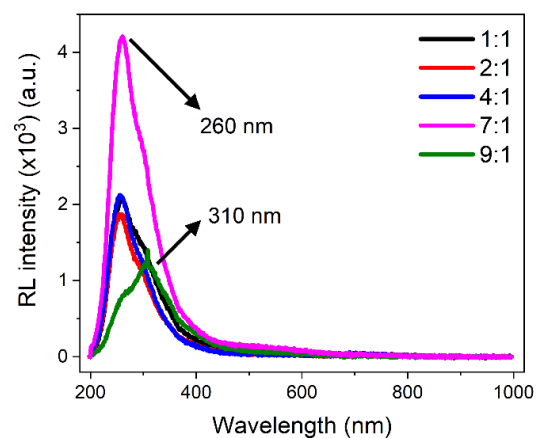

Figure 3. RL emissions of BeO pellets are produced by different EG:CA ratios in sol-gel synthesis.

To examine the effect of different EG:CA ratios on the TL signals of BeO, after a beta dose of 1 Gy, the samples were heated up to 650 °C at a heating rate of 3 °C/s and the resulting TL glow curves are presented in Figure 4. As can be seen from the figure, the TL signals of BeO produced with different EG:CA ratios present significant differences. The increase observed in the TL signals of the samples with increasing EG:CA ratio ended with a ratio of 7:1. Although the 9:1 ratio also caused an increase in TL signals, it caused a decrease in the sensitivity of TL traps located in the high temperature region, defined as deep traps. In dosimetric measurements, it can be said that the most appropriate EG:CA ratio for the region of luminescence signals after 200 °C, which can be considered thermally stable, is 7:1. Undoubtedly, more detailed further research studies are needed.
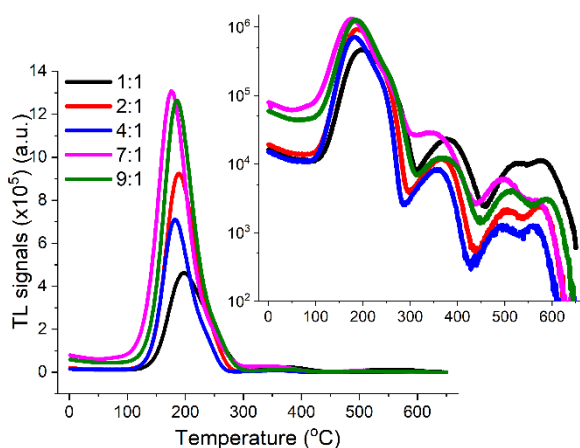

Figure 4. TL glow curves of BeO pellets produced by different EG:CA ratios in sol-gel synthesis. Inset figure: TL glow curves of BeO in semi log-scale for better illustration of high temperature peak regions.

To examine the effect of different EG:CA ratios on the OSL signals of BeO, after a beta dose of 1 Gy, the samples were exposed to 200 s of blue light LED stimulation and the obtained OSL signals are presented in Figure 5. As can be seen from the figure, the OSL signals of BeO produced with different EG:CA ratios showed differences. With increasing EG:CA ratio, maximum OSL signals were obtained from the sample developed with a 7:1 ratio. In general, it can be said that OSL signals consist of two parts, which decay rapidly in the first 25 s and then continue slowly until 200 s. On the contrary, regarding the slowly decaying component, it is evident that sensitivity enhances with increasing EG:CA ratios. This indicates that increased densities of gelling agents stimulate the slow decay process and consequently prolong luminescence lifetimes. It should be noted that further in-depth studies are needed to prove this.
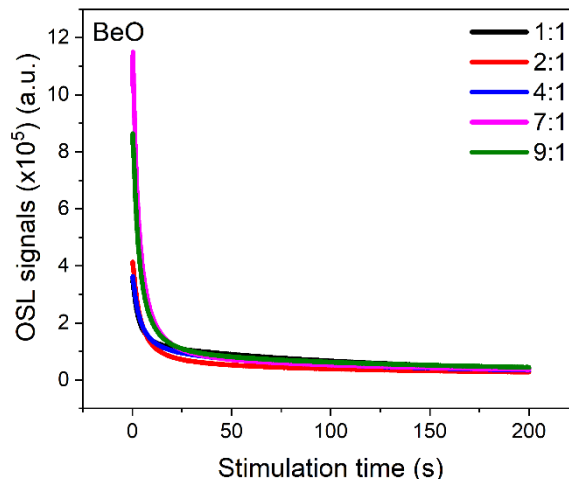

Figure 5. OSL decay curves of BeO pellets produced by different EG:CA ratios in sol-gel synthesis.

3. Conclusion

In this study, BeO powders were produced by the sol-gel synthesis method and the effects of changing the ratios of ethylene glycol (EG) and citric acid (CA), the gelling agents used during production, on the structural, morphological and luminescence properties of the final products were examined. Changes in the structure and morphology of BeO due to varying EG:CA ratios presented that the 7:1 ratio was most appropriate ration for luminescence measurements. Additionally, RL emission bands showed increases in luminescence intensities in the range of 200 to 400 nm, and TL and OSL signals obtained in the UV region supported these results. This study has laid a solid foundation for future research by defining the relationship between the application of optimum conditions for gelling agents and luminescence efficiency, a critical step for the sol-gel synthesis of BeO.

Method

Beryllium oxide (BeO) ceramics were synthesized using the Sol-Gel synthesis method. Firstly, beryllium sulfate tetrahydrate ($BeSO_4 \cdot 4H_2O$) was choosed as the starting salt and weighed. Then, mixtures were prepared using Ethylene Glycol (EG) and Citric Acid (CA) in different proportions. The ratios of EG and CA were selected as 1:1, 2:1, 4:1, 7:1, and 9:1, respectively. $BeSO_4 \cdot 4H_2O$ starting salt was mixed with EG and CA and this mixture was thoroughly homogenized. The resultant gel was dried at 80 °C, during which water evaporated and a gel matrix was formed. Next, the calcination step was applied at 1000 °C for 4 h. This process transforms the starting salt into ceramic material. Finally, the sintering process was applied at 1600 °C for 2 hours. This step helped improve the

crystal structure of the material and gain the desired ceramic properties.

The crystal structures of beryllium oxide (BeO) ceramics synthesized using different EG:CA ratios were characterized using X-ray diffraction patterns (XRD). Diffraction analysis was performed using Cu-Kα radiation (40 kV, 30 mA) with the Rigaku SmartLab Diffractometer. Patterns between 20° and 80° of angle 2θ were scanned in 0.02° increments. Phase identification was made regarding PDF card 98-016-3468 provided by the International Center for Diffraction Data (ICDD). Additionally, the surface morphology and grain sizes of the materials synthesized by sol-gel method were also examined. For this purpose, Zeiss Supra 55 FE-SEM (Field Emission Scanning Electron Microscope) was used. Micrographic images were obtained by FE-SEM with a spectral slit width of 1.5 nm at room temperature. The presented micrographic images were taken at 5000x direct magnifications, 20 kV, and 2.5 dot size.

Luminescence characterizations of the materials obtained after the synthesis and pellet preparation processes were carried out using Thermoluminescence (TL) and Optical Stimulated Luminescence (OSL) techniques. These characterization studies were carried out using a ^{90}Sr-^{90}Y beta radiation source and a bialkaline model 9235 QA photomultiplier tube (PMT) was used for detection. Beta dose rate of the reader used in this study was 0.15 Gy/s. Stimulation was performed through a DA-20 model RisØ TL/OSL reader system with blue LEDs (λ ∼ 470 nm). To detect TL/OSL signals in the UV region, a Hoya U-340 nm filter was used in front of the PMT. In OSL measurements, BeO pellets were irradiated with beta doses of 0.5 Gy and preheated at 100 °C for 10 s. OSL readings were performed using 200-second blue light stimulations in continuous wave OSL mode (CW-OSL) at room temperature. TL measurements were made by initially heating 0.5 Gy irradiated pellets up to 650 °C with a heating rate of 3 °C/s, starting from room temperature, without preheating. Radioluminescence (RL) emissions of BeO pellets were obtained using a hand-built X-ray Luminescence system with a 4-40 kV X-ray tube and a USB-2000 model Ocean Optics fibre spectrometer manufactured for low-sensitivity applications.

Acknowledgements

Conflicts of Interest

The author stated that did not have conflict of interests.

Author Contributions

VA: Performed experiments/data collection, data analysis and interpretation, drafted the paper, provided grammatical revisions to manuscript, provided revisions to scientific content of manuscript.

Data Availability Statement

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

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