JOURNAL OF MATERIALS SCIENCE **32** (1997) 2791–2796

Review
Thermoluminescence dosimetric properties of beryllium oxide

D. R. VIJ, N. SINGH
Department of Physics, Kurukshetra University, Kurukshetra 136 119, India

Beryllium oxide (BeO) displays strong thermoluminescence (TL) together with tissue - equivalent properties which underline its application as a TL dosimeter. In the dosimetry of X- and γ-rays some of the advantages of BeO over other TL materials are its commercial availability, low cost, chemical inertness, non-toxicity (as a ceramic), high sensitivity to ionizing radiations, good reproducibility of response, low fading, absence of low-temperature peaks and moderate energy dependence. Various authors have reported glow curves of BeO TL phosphor, whose dominant dosimetric peak lies between about 160 and 200 °C. The position of this peak, however, depends upon the type of the radiation used for exciting the phosphor. Although fading of TL is nominal when kept in the dark, the γ-exposed BeO phosphors fade faster when exposed to ambient light. When exposed to γ-radiation, these phosphors exhibit linearity from a minimum of about 1 mrad (1 rad $=10^{-2}$ gray) up to approximately 10 rad, above which there is supralinear behaviour, and the concentration of impurity ions in BeO is reported to expand the linearity region. Ceramic samples have been reported to exhibit a roughly flat response when exposed to X-rays of 30–115 keV and γ-rays of ^{60}Co. Because their response to thermal neutrons is negligible compared to the γ-response, the use of BeO has been suggested to measure the γ-component in the (n, γ) mixed fields.

1. Introduction

High melting point (2570 °C) beryllium oxide (BeO) ceramics are refractory materials having high electrical resistivity ($> 10^{13}$ Ωcm), high thermal conductivity (as high as that of aluminium), a wide band gap of about 10.6 eV [1], and a low thermal neutron cross-section (10 mb). These properties render them suitable for use in refractory ware, as heat sinks for electronic devices and as high-efficiency moderators and reflectors in nuclear reactors. BeO also displays strong TL together with tissue-equivalent ($Z_{\text{eff}} = 7.1$) properties which underline its application as a TL dosimeter.

In the dosimetry of X- and γ-rays, some of the advantages of BeO over other TL materials are their commercial availability, low cost, chemical inertness, non-toxicity (as a ceramic), resistance to mechanical shocks, low fading, the absence of low-temperature peaks and moderate energy dependence. The low neutron sensitivity makes the application of BeO promising in mixed γ-neutron radiation fields, primarily as an inexpensive nuclear accident dosimeter [2].

However, these phosphors have some disadvantages, i.e. they emit a small amount of tribo-TL and possess a characteristic light-stimulated fading which can be overcome by precautions when handling preferably in red or yellow light. BeO is highly toxic when used in powder form but, on the other hand, completely harmless when used in the form of sintered pellets and chips. This paper reviews the various TL and dosimetric properties of BeO phosphors leading to their applications in radiation dosimetry.

2. Preparation methods

BeO is commercially available in the undoped form under the commercial name “Thermalox 995” manufactured by Brush Beryllium Co., Elmore, OH, USA, with a total content of impurities not exceeding 0.5% [3], the major impurities being, 2150 p.p.m. Si, 945 p.p.m. Mg, 100 p.p.m. Fe, 60 p.p.m. Ca and 55 p.p.m. Al. After igniting a mixture with a proper mineralizer, the amorphous BeO is transferred into a micro-crystalline state (hexagonal wurtzite structure) which is further sintered under high temperature and pressure. Tomita and Tsutsumi [4] used BeO ceramics (obtained from NGK Insulator Ltd, Japan) with impurities of silicon and calcium (100 p.p.m.), sodium (50 p.p.m.), magnesium, iron and nickel (20 p.p.m.).

Yamashita *et al.* [5] prepared lithium and sodium-doped BeO, i.e. BeO (Li 0.5 mol %) and BeO (Na 0.5 mol %). Purified BeO powder and a small quantity of dopant powder were mixed in proper ratio. The dopant materials used were SiO_2, GeO_2, $Al_2(SO_4)_3$ and Na_2SO_4. The mixture was press-formed into rod

0022–2461 © 1997 Chapman & Hall

and disc shapes, sintered at a temperature of more than 1500 °C and cooled slowly. As a dosimeter sample, glass-encapsulated ampoules were prepared, because ceramic samples without surface treatment were often soiled by dust or repeated use. The ceramics were ground into small grains, 100–300 μm in diameter, and sealed into a glass ampoule.

BeO discs were prepared by Scarpa [6] in three different grades:(1) slip cast (SC), (ii) hot-pressed (HP) and (iii) nuclear quality (NQ), depending upon their method of sintering, density and chemical purity. The SC grade was sintered without pressure and its normal density was 2.2 gcm^{-3}. The density of HP and NQ types was higher, reaching 2.8 gcm^{-3}. The main impurities were silicon, sodium, fluorine, sulphur and carbon, their typical impurity levels in SC and HP being 0.4% but only 25 p.p.m. for NQ.

Kortov *et al.* [7] have prepared and studied several types of commercial BeO ceramics with a view to their possible application in TL and/or ESR dosimetry. The best results were obtained with optically transparent high-density ceramics with little tendency to sputtering, simultaneously doped with lithium and neodymium ions and having no pyroelectrical effects during heating and cooling. A mixed BeO:TiO$_2$ ceramic, showing high electrical conductivity, has been subjected to preliminary investigation with regard to its application in thermally stimulated exoelectron emission(TSEE) and TL dosimetry [8] . The two oxides have been observed to construct independent substructures in the mixed ceramic. The TiO$_2$ substructure provides electrical conductivity, and was passive from the TL and TSEE point of view, whereas the BeO substructure was found to be fully responsible for the dosimetric signals.

3. TL and dosimetric characteristics

The calculated effective atomic number, Z_{eff}, of BeO is 7.1 compared to 7.5 for water and soft tissue [9].

3.1. Glow curves

BeO:Li (0.5 mol %) and BeO:Na (0.5 mol %), prepared by Yamashita *et al.* [5], show glow peaks at 180 °C. The curve shape does not vary for exposure levels between 1 mrad(1 rad =10^{-2} Gy) and several hundred rad. At more than 1000 rad, the glow curve changes and a new peak appears at about 210 °C.

Hobzova [10] noticed three peaks in BeO (at 50, 190 and 280 °C) when excited by β-rays and only two peaks at 190 and 280 °C when excited by ultraviolet light (Fig. 1). Busuoli and Julius [11] also observed glow curves in BeO with two distinct maxima at ~180 and ~280 °C and the third at 60 °C. Lakosi *et al.* [2] have shown that the glow curve of BeO displays two peaks; one at about 200 °C and the other ~360 °C. The position of the first peak depends on the dose value. For higher doses the first peak shifts to 260 °C making it a dominant peak, whereas the peak at 360 °C is reduced to a negligible value.

When excited by X-rays (~1.5 x 10^3 rad dose), glow curves occur at 150 and 260 °C [4] which are roughly in agreement with most of the reported results on various BeO samples. However, the structure of the glow curves depends upon the preparation parameters, such as concentration of impurities and the magnitude of the absorbed dose.

Scarpa [6] showed the effect of the physical form of the BeO dosimeter on its TL. High-temperature glow peaks at ~530 and 630 °C have also been observed in "Thermalox 995" tablets when irradiated by β-particles and X-rays (dose ~180 Gy) [12]. TL of BeO has been reported to have two well-separated peaks at 222 and 369 °C [13]. The activation energy values, found using different measurement methods, were in good agreement. A kinetic order of about two has been determined for the first peak, whereas the second peak follows first-order kinetics.

BeO exhibits TL emission from the blue region of the visible spectrum to the ultraviolet up to the lower limit of 200 nm [4, 5, 9, 11, 12, 14–16] (Fig. 2) which depends upon the nature of the glow curve. Different glow peaks show different TL emission spectra. This implies that to obtain maximum sensitivity, BeO must

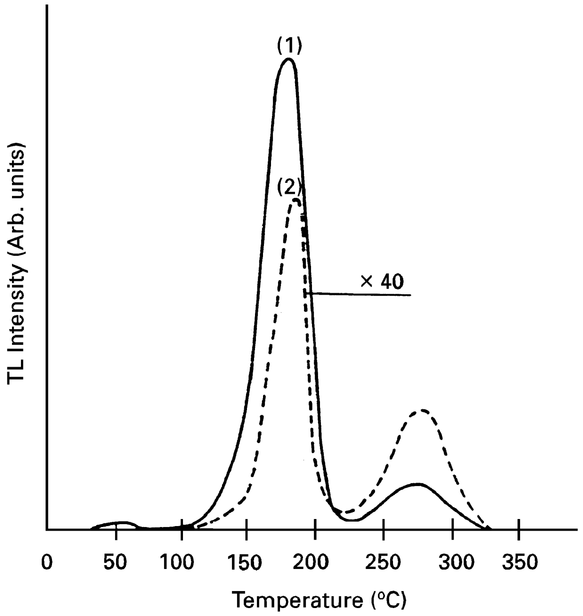

Figure 1 Glow curves of (1) BeO (Thermalox 995) irradiated to 700 rad of β-rays and (2) BeO exposed to ultraviolet light for 5 min [10]. (*Permission granted by Health Physics*).

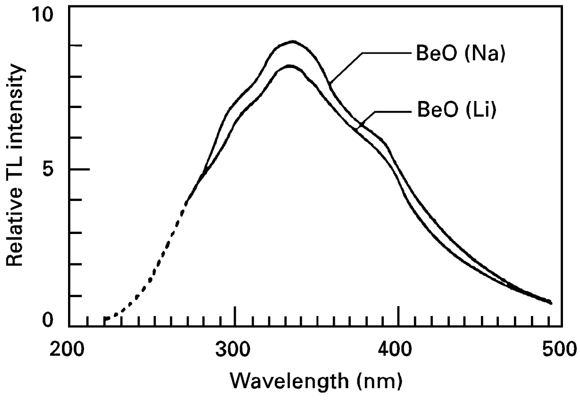

Figure 2 TL emission spectra of BeO (Li) and BeO(Na) observed after being exposed to ^{137}Cs γ-rays at 1000 rad [5]. (*Permission granted by Health Physics*).

be read using ultraviolet-sensitive PM tubes, quartz windows and ultraviolet-transmitting filters. Spectral luminescent characteristics of aggregate colour centres, in BeO crystal, produced by high-dose neutron irradiation and special heat treatment, have also been reported [17]. Characteristics of the relaxation process at doses in the dosimetric region of BeO TL dosimeter have been given by Ogorodnikov *et al.* [18]. Synchronous measurements of the TSL and TSEE on heating in a linearly oscillating mode yielded the temperature dependence of the mean thermal activation energies and of the kinetics and amplitudes of the luminescence and exoemission during the temperature oscillations. Redistribution of electronic excitations among competing relaxation channels has also been discussed.

3.2. Thermal annealing

To remove residual dose, various annealing treatments have been described by different workers. Crase and Gammage [19] annealed "Thermalox 995" at 650 °C for 30 min, followed by a slow cooling to room temperature. For low exposures, up to a few rad, the readout process anneals the dosimeter which can be reused without any additional heat treatment. Scarpa *et al.* [16] used annealing at 600 °C for 5 min which could be omitted following irradiation below 1 rad, without large changes in precision. According to Yamashita *et al.* [5], for BeO(Li) and BeO(Na) samples, after repeated use, easy annealing at 450-500 °C for 1–10 min removes the residual doses. The TL efficiency remains unchanged after more than 100 cycles of repeated exposure and readout operations. However, BeO annealed at higher temperature (about 800 °C), after pre-exposure, to empty all the traps, was not found to be sensitive to ultraviolet light [10].

Practically, the sensitivity and reproducibility of a TL detector depends on the annealing procedures. When these are simple the detector is certainly more convenient [14]. This is contrary to the result of Lakosi *et al.* [2] that, apart from a photostimulation effect, BeO is not sensitive to annealing. The detector sensitivity is preserved even after several anneals. The accuracy of the exposure measurement can be accepted for personnel dosimetry, with the remark that the technique is not suitable for energies below 20 keV [20].

Effects of varying the cooling rate during annealing in BeO TLDs have been investigated by Borio *et al.* [21]. The uncertainity associated with TL measurements has been related to the heating phase of the annealing, and of the reading cycles, in particular; the need for stability of the ovens and the reproducibility of the heating rate during TL readout has been pointed out. The cooling conditions have been found to be another element of importance in the annealing cycles of some TL materials. Slow cooling markedly increased sensitivity of BeO. Field fluctuations have been found to alter the energy structure of the traps in BeO single crystals [22]. Two types of field fluctuations, which lower and raise the potential barrier, respectively, have been reported. It has been shown that the effects of spontaneous emission are responsible for the poor reproducibility of dosimetric information in TL and thermo-exoemission dosimeters that employ BeO.

Busuoli *et al.* [23] have reported that it is possible to make BeO more sensitive to low doses by its heat treatment at 1000 °C for 15 h. This treatment also improves the reproducibility of the TL signal at low doses. Scarpa *et al.* [16] also found that heat treatment at 1500 °C for 2 h gives a 20%–40% increase in sensitivity.

Gammage and Checka [24] have shown that heating BeO discs at 1320 °C in air for 500 h in alumina crucibles increases the TSEE sensitivity while seriously affecting the TL. This sensitization is said to be related to production of the surface compound 2BeO, SiO_2 [25], silica being an impurity present in bulk concentration of 2000 p.p.m.

3.3. Fading

Scarpa [6] investigated short-term fading, with readouts at various intervals after an irradiation of 100 rad. The samples were stored in the dark at room temperature. The HP beryllium oxide exhibited fading of about 20% in 3 days, which can be attributed to the low temperature of its first two peaks (70 and 160 °C). The other two types of BeO show no significant fading after an initial 3%–4% drop during the first 24 h. When kept in dark at room temperature, fading in BeO(Li) is less than 20% within the first hour and 8% within the following 30 days, after having been exposed to 10 rad γ-rays, whereas it is less than 10% within the first hour and 5% within the following 30 days in the case of BeO(Na). Fading of γ-ray-exposed BeO(Na) and BeO(Li) is less than 10% for a light exposure of 300 lux for 10 min; however, it reached almost 90% in 1 day [5]. According to Crase and Gammage [19], fading of the main TL peak (167 °C) occurs quite rapidly, the decay being 50% in 30 min under laboratory lighting. The higher temperature TL peak (276 °C) is much more resistant to bleaching with a 20% loss after 48 h. However, when stored in the dark at 30 °C and a relative humidity of 90%, the decay is about 10% in 3 months.

Lakosi *et al.* [2] noted a fading of 8% during a period of 2 weeks when the samples were kept in the dark, and Benincasa *et al.* [9] observed some fading after a period of 2 months, but the fading was much faster if irradiated BeO discs were exposed to ambient light. A 50% decay is reached after only 20–30 min with light intensities of 1500–3000 lux. Other authors [26, 27] have provided fading rates ranging from 0% in 5 months to 8% in 7 months; this spread in the results depends upon the type of material used, annealing treatments and the techniques followed to carry out the measurement. Because of rapid fading of TL in BeO with laboratory fluorescent light or daylight, BeO detectors must be protected from light during readout processes in order to avoid systematic errors in the dose assessment. This necessitates the use of red light when handling "Thermalox 995" detectors which are kept in black paper and/or red perspex [28].

3.4. Dose response

3.4.1. Linearity, supralinearity and sensitization

Scarpa [6] tested all qualities of beryllia under the doses of γ-radiation ranging from 10–10 000 rad. Supralinearity starts around 100 rad and tends to saturate above 10 000 rad. In the very low exposure region, a slight sublinearity seems to be present [9]. This behaviour agrees substantially with the results of Tochilin *et al.* [29] but differs with that of Crase and Gammage [19] in which case the intensity of the main TL peak (167 °C) increases linearly with γ-ray exposure from a minimum of about 1 mrad up to approximately 10 rad, above which there is supralinear behaviour [19] (Fig. 3).

The dose response of the two TL peaks (200 and 360 °C) has been reported by Lakosi *et al.* [2]. The ratio of the two peak heights rapidly increased to the advantage of the first peak with increasing doses. The second peak was not perceptible above 5000 rad. The supralinearity of the response is attributed entirely to the first peak. The second peak did not increase linearly with increasing doses. It tended towards saturation above 5000 rad. Consequently, if the second peak was also taken into consideration during evaluation, a less pronounced supralinearity will be obtained. Lakosi *et al.* [2] found that above 150 krad the TL response became saturated and the samples exhibited a greyish brown colour. The colour disappeared after the reading. The sensitivity of the dosimeter was found to vary with the exposure dose (Fig. 4). Supralinearity has been assigned to new traps occurring at higher doses and to the corresponding new peaks in the glow curve.

Yamashita *et al.* [5] observed that exposure response of BeO(Li) is linear from 1 mrad to 500 rad and that of BeO(Na) from 2 mrad to 100 rad. According to them, the concentration of ions also expands the linearity regions. For instance, BeO (5 mol % Li) was linear up to 2000 rad, and BeO (5 mol % Na) was linear up to 1000 rad. BeO can detect exposure up to 10^5 rad [2, 19, 30, 31].

3.4.2. Energy dependence

The energy response of "Thermalox-995" has been observed by Crase and Gammage [19] using heavily filtered X-rays and γ-rays. They found that LiF (TLD-100) behaves quite similarly to BeO TLD. According to Yamashita *et al.* [5], ceramic samples of both BeO(Li) and BeO(Na) have roughly a flat response (within an experimental error of ± 15%) when exposed to X-rays of 30–115 keV and γ-rays of ^{60}Co. Samples encapsulated in glass ampoules have an over-response as large as 30% for an exposure of X-rays of 30–110 keV.

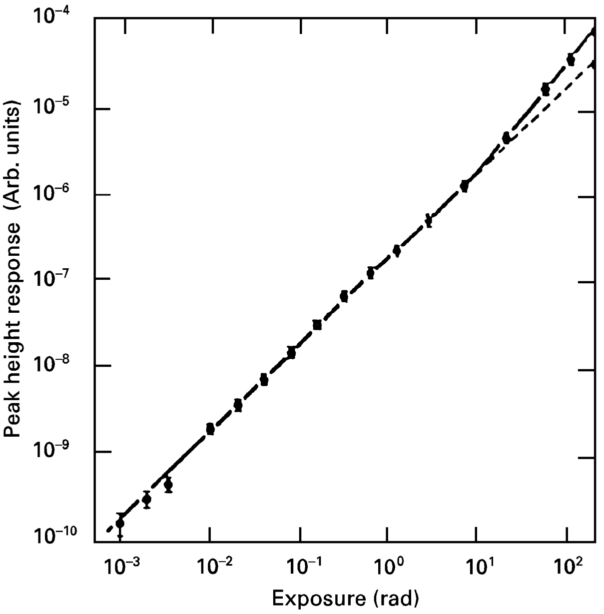

Figure 3 Response of 12.7 mm diameter "Thermalox 995" as a function of ^{137}Cs gamma exposure [9].

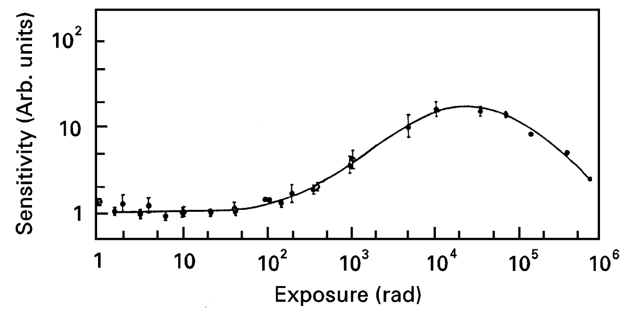

Figure 4 Sensitivity versus exposure [2]. (*Permission granted by Health Physics*).

BeO response to the same exposure value depends on the radiation energy. For example, BeO exposed under electronic equilibrium conditions has a response 1.6 times higher at 80 keV than at ^{60}Co [19, 29, 31, 32]. Fig. 5 shows the detector energy responses, normalized to ^{60}Co γ-rays [20]. Curve B, relative to the filtered detector, is flat only in the range from 300 keV to ^{60}Co; at lower energies the response increases up to 1.3 at 150 keV and then decreases steeply. The response of the second detector (curve A) has its maximum at 70 keV. The ratio of the ordinates of the two curves of Fig. 5 is shown in Fig. 6. It is possible to estimate the energy of the incident radiation from this figure.

3.4.3. Neutron response

As the TL response of BeO to thermal neutrons is negligible compared to the γ-response, the use of BeO enables good measurement of the γ-component in the (n, γ) mixed fields unless the thermal neutrons are prevalent in the field [29]. For this use, the lower the sensitivity to fast neutrons, the far simpler the glow curve and the better energy independence, giving a distinct advantage to BeO [16].

3.4.4. Photo-transfer thermoluminescence (PTTL)

BeO, previously irradiated by ionizing radiation, gives a TL signal after ultraviolet illumination and is

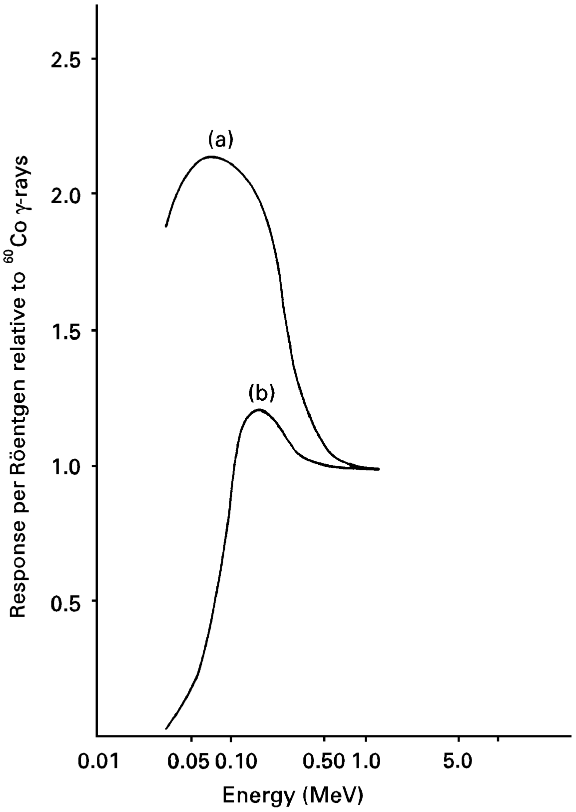

Figure 5 Energy responses of the detectors : (a) unfiltered detector, (b) filtered detector [20] (*Permission granted by Health Physics*).

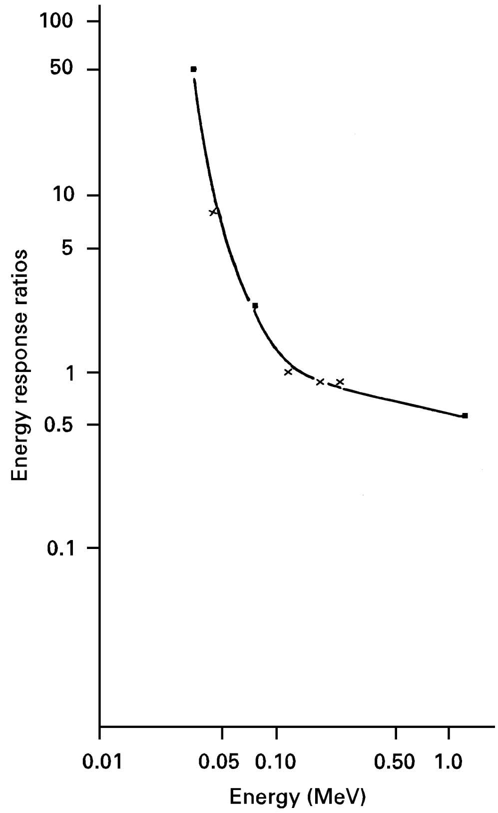

Figure 6 Monitoring curve of the energy response ratios [20].

proportional to the ionizing radiation dose which can be re-assessed by PTTL [10]. The PTTL and optical bleaching properties of BeO detectors have been investigated by Lembo *et al.* [33] as a possible technique for the epidemiological studies of solar ultraviolet radiation-induced skin cancer. The ultraviolet-induced bleaching of the TL glow signal, as well as the phototransfer of the second readout, have been investigated as a function of ultraviolet exposure.

The photostimulation effect is stronger if the samples are not annealed and this effect disappears in the case of annealing above 600 °C [34]. According to Lakosi *et al.* [2], BeO samples previously irradiated to 100 rad and without annealing, were exposed to sunlight for 10 min after readout, and 10%–12% of the initial TL could be recorded again, but annealing was found to be necessary only for measuring the ultraviolet-induced TL response [10].

3.4.5. Self-absorption of TL light

An experimental procedure for the determination of the self-absorption coefficient of TL light in BeO “Thermalox 995” chips has been described [35]. It has been emphasized that the self-absorption effect should be considered when comparing the TL readouts measured with BeO detectors of different thickness.

4. Conclusion

BeO has strong thermoluminescence and tissue-equivalent properties. This has been put to commercial use in the dosimetry of X- and γ-rays and mixed (n, γ) fields. However, in spite of the vast amount of published work, the results seem to be subjective, in that no standard set of conditions has been prescribed for preparation, storage, handling, annealing, etc., to give an international character to the dosimeters based on BeO ceramic. The controversial phenomenon of self-absorption of TL light, reported in BeO by Lembo *et al.* [35], needs further investigation because it may provide a definite answer to this unsolved problem.

References

1. V. Y. IVANOV, V. A. PUSTOVAROV, A. V. KRUZHALOV and B. V. SHULGIN, *Nucl.Instrum. Meth. Phys. Res. A. Accel. Spectrum. Detect. Assoc. Equip.* (Netherlands) **A 282** (1989) 559.
2. L. LAKOSI, P. P. SZABO and S. MAKRA, KFKI-75-10 report of Central Research Institute for Physics, Budapest, Hungary, (1975).
3. Z. SPURNY, and L. HOBZOVA, *Radiochem. Radioanal. Lett.* **29** (1977) 287.
4. A. TOMITA and K. TSUTSUMI, *Jpn J. Appl. Phys.* **18** (1979) 397.
5. T. YAMASHITA, Y. YASUNO and M. IKEDO, *Health Phys.* **27** (1974) 201.
6. G. SCARPA, *Phys. Med. Biol.* **15** (1970) 667.
7. V. S. KORTOV, S. J. MILMAN, A. I. SLESAREV and V. S. KIJKO, *Rad. Prot. Dosim* **47** (1993) 267.
8. V. S. KORTOV, S. J. MILMAN, A. I. SLESAREV, A. SURDO, J. LESZ and K. S. LESZ, *ibid.* **47** (1993) 599.
9. G. BENINCASA, L. CERAVOLO and G. SCARPA, Comitato Nazionale Energia Nucleare (Italy), RT/PROT (74) 1.
10. L. HOBZOVA, in “Proceedings of the 4th International Conference on Luminescence Dosimetry, Krakow, Poland (edited by T. Niewiadomski, 1974) p. 1081.
11. G. BUSUOLI and H. W. JULIUS, in “Proceedings of the 5th International Conference on Luminescence Dosimetry, Sao Paulo, Brazil (edited by A. Scharmann, 1977) p. 225.

12. L. HOBZOVA, *Phys. Status Solidi* (*a*) **60** (1980) K207.
13. C. BACCI, P. BERNARDINI, A. DAMILANO, C. FURETTA and B. RISPOLI, *J. Phys. D Appl. Phys.* (*UK*) **22** (1989) 1751
14. C. E. MANDEVILLE and H. O. ALBERCHT, *Phys. Rev.* **94** (1954) 494.
15. Z. SPURNY and J. HRUSKA, *Phys. Med. Biol.* **21** (1976) 439.
16. G. SCARPA, G. BENINCASA and L. CERAVOLO, in "Proceedings of the Symposium on Dosimetry in Agriculture, Industry, Biology and Medicine, IAEA, Vienna (1973) IAEA-SM-160/39.
17. I. N. ANTARYGIN, S. V. GARBUNOV, A. V. KRUZHALOV and S. V. KUDYAKOV, *J. Appl. Spectrosc.* **56** (1992) 250.
18. I. N. OGORODNIKOV, V. I. KIRPA and A. V. KRUZHALOV, *Sov. Phys. Tech. Phys.* (USA) **36** (1991) 759.
19. K. W. CRASE and R. B. GAMMAGE, *Health Phys.* **29** (1975) 739.
20. G. BUSUOLI, I. SERMENGHI, O. RIMONDI and G. VICINI, *Nucl. Instrum. Meth.* **140** (1977) 385.
21. R. BORIO, S. CHIOCCHINI, U. MAIO, P. D. ESPOSTI, L. LEMBO, M. PIMPINELLA, R. POLI and S. SCAMPOLI, *Rad. Prot. Dosim.* (*UK*) **33** (1990) 197.
22. I. N. OGORODNIKOV, V. I. KIRPA and A. V. KRUZHALOV, *Tech. Phys.* (*USA*) **38** (1993) 404.
23. G. BUSUOLI, R. NANNI and I. SERMENGHI, (Rad. Prod. Laboratorio Fisica, CNEN, Bologna, Italy), 1981 p. 1.
24. R. B. GAMMAGE and J. S. CHECKA, *Health Phys.* **30** (1976) 311.
25. R. B. GAMMAGE, K. W. CRASE and K. BECKER, *ibid.* **22** (1972) 57.
26. M. BOEHM, E. PITT and A. SCHARMANN, *Rad. Prot. Dosim.* **8** (1984) 139.
27. J. B. O. HAGAN, A. J. PEARSON and C. M. H. DRISCOLL *ibid.* **17** (1986) 347.
28. B. A. HENAISH, A. M. SYED and S. M. MORSY, *Nucl. Instrum. Meth.* **163** (1979) 511.
29. E. TOCHILIN, N. GOLDSTEIN and W. G. MILLER, *Health Phys.* **16** (1969) 1.
30. *Commission of European Communities*, *Report* EUR 5358 (1975).
31. G. SCARPA, G. BENINCASA and L. CERAVOLO, in "Proceedings of the 3rd International Conference on Luminescence Dosimetry" Riso (edited by V. Mejdhal, 1971) p. 427.
32. G. BUSUOLI, O. RIMONDI and G. VICINI, *Doc. CEC* **73** (1973) 9.
33. L. LEMBO, M. PIMPINELLA and B. MUKHERJEE, *Rad. Prot. Dosim.* **33** (1990) 201.
34. Y. YASUNO and T. YAMASHITA, in "Proceedings of the 3rd International Conference on Luminescence Dosimetry" Riso (edited by V. Mejdhal, 1971) p. 290.
35. L. LEMBO, M. PIMPINELLA and B. MUKHERJEE, *Rad. Prot. Dosim.* **33** (1990) 43.

Received 10 August 1995
and accepted 9 September 1996