



AMPT'01

**International Conference
on
Advances in Materials and
Processing Technologies**

**September 18-21, 2001
Leganés, Madrid, Spain**

FINAL PROGRAMME

ROOM 5: (Code 4.1.E.05)

Session Title: Ceramics 3

Chairs: L. CATARINO and A. VÁREZ

11:30 Keynote Lecture

Ordering induced by wet processing in ceramic-metal systems

J.S. Moya, S. López-Esteban, M. Díaz, F. Esteban, J.F. Bartolomé, J. Requena, C. Pecharromás

12:00 *Microstructural Engineering of Functionally Graded Materials by Electrophoretic Deposition*

S. Put, J. Vleugels and O. Van der Biest

12:15 *Chrysotile as catalyst in the degradation of cationic and non ionic surfactants in aqueous solutions*

A. Fachini, I. Joeke

12:30 *Nanocrystalline SnO₂ obtained by means of a microwave process for gas sensing applications*

A. Cirera, J. Arbiol, A. Cornet and J.R. Morante

12:45 *Convertible compounds as negative electrodes for lithium batteries*

M. Martín-Gil M., A. Kuhn., F. García-Alvarado and A. Várez.

13:00 *Effect of dopants in the luminescent properties of synthetic quartz for dosimetric purposes*

V. Correcher, J. García-Guinea, L. Sánchez-Muñoz, A. Delgado.

13:15 *A New Method for Processing of Strontium Hexaferrite with Enhanced Magnetic Properties*

S.A. Seyyed Ebrahimi

LUNCH

EFFECT OF DOPANTS IN THE LUMINESCENT PROPERTIES OF SYNTHETIC QUARTZ FOR DOSIMETRIC PURPOSES.

V. Correcher*, J. García-Guinea**, L. Sánchez-Muñoz***, A. Delgado*

*CIEMAT. Av. Complutense 22. Madrid 28040 Spain

**Museo Nacional de Ciencias Naturales (CSIC). C/ José Gutiérrez Abascal 2 Madrid 28006 Spain.

***Dpto. Química Inorganica. Univ. Jaume I. Borriol. Castello 12080 Spain.

Corresponding author: V. Correcher Fax +34 91 3466005; Phone +34 91 3466322.

E-mail: v.correcher@ciemat.es

ABSTRACT: Quartz obtained from structural materials (bricks, tiles, etc.) is often employed as a dosimeter using the thermoluminescence (TL) technique in the field of dating and retrospective dosimetry. As known, the TL response depends on the impurities in quartz lattice. For this motive, some members of β -quartz series were synthesised using the ceramic method from precursor powders $\text{-Li}_2\text{CO}_3$, $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Si(C}_2\text{H}_5\text{O)}_4$ - with different compositions, to create standard materials. The lattice of aluminosilicates consists of chains of SiO_4 and AlO_4 tetrahedra forming spirals or rings. The Al^{3+} ions are replacing Si^{4+} and a positive charge is needed (trapped holes or Na^+ , K^+ , Li^+ , etc. cations). The Li^+ ions are placed in void channels inside the spirals of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra. Here some characteristic features of the TL signal in three of β -quartz with different concentrations of lithium-aluminium were measured in the UV-blue region of the spectrum. Irradiated β -quartz samples display high linearity - one of the main features of a dosimeter - after additional radiation doses (from 0.5 to 5 Gy).

Keywords: Thermoluminescence, Synthetic quartz, Retrospective Dosimetry

1 INTRODUCTION

The luminescent properties of quartz, used as the main dosimetric material, have been usually employed in retrospective dosimetry [1], archaeological and geological dating [2], detection of food irradiation [3], etc. The quartz emission relies on the most important features required for a dosimeter, i.e. to be highly sensitive, reproducible, to possess low fading and good dose linearity in the ranges of interest.

However, it is not possible to find pure quartz in natural environments; different concentrations of impurities (mainly Li and Al) are displayed in the lattice, modifying some of the typical characteristics of the thermoluminescence (TL) emission (such as intensity or position of the TL glow peak). If no ion substitutes the Si, the framework is SiO_2 and all valence bonds are satisfied. Al ions frequently substitute the Si in the tetrahedra and interstitial monovalent or sometimes divalent cations (Li^+ , Na^+ , K^+ , Ca^{++}) are required to preserve charge balance. The Li^+ ions are placed in void channels within the spirals of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra. The role of $[\text{AlO}_4]^\ominus$ centres in the blue thermoluminescence of quartz was described by Martini et al. [4] who demonstrated prolonged high-temperature annealing of samples reduces the presence of ionic charge compensators and creates luminescence traps. This is crucial as in both, dating and retrospective dosimetry, the analytical routines used are based on luminescence methods (blue emissions around the 400nm) involving thermal treatments.

In this paper, TL differences observed in three different synthetic quartzes grown with different content of Li and Al impurities (LiAlSiO_4 , $\text{LiAlSi}_5\text{O}_{12}$ and $\text{LiAlSi}_{16}\text{O}_{22}$) are studied. Dose response of samples was analysed in the UV-blue spectral region (380nm) to determine the suitability of these materials as potential dosimeters for environmental dose reconstruction.

2 MATERIALS AND METHODS

Lithium-aluminium stuffed derivatives of silica polymorphs, mixture of tetragonal β -spodumene (LiAlSiO_4) and hexagonal β -eucryptite ($\text{LiAlSi}_{16}\text{O}_{22}$) were synthesised by Hamilton and Henderson's gelling method [5]. The elements (Li, Al, Si) were introduced from precursor powders, in three steps: i) Lithium from Li_2CO_3 , ii) Silica as TEOS which is tetraethylorthosilicate ($\text{Si}(\text{C}_2\text{H}_5\text{O})_4$) and iii) Aluminium as crystals of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Al and Li cations were introduced in stoichiometric proportions to maintain the electrical neutrality of the quartz lattice ($\text{Al}^{3+} + \text{Li}^+ = \text{Si}^{4+}$). The samples studied were LiAlSiO_4 , $\text{LiAlSi}_5\text{O}_{12}$ and $\text{LiAlSi}_{16}\text{O}_{22}$.

The structural data of the analysed samples were assessed by a Siemens D-5000 X-ray automated diffractometer using the K_α radiation of Cu with a Ni filter at a setting of 40kV and 200 mA.

These samples were carefully crushed with a pestle in a mortar and sieved to obtain a grain size fraction of 50-90 μm . TL measurements were made using an automated Risø TL system model TL DA-12 manufactured by Risø National Laboratory [6]. This reader is provided with an EMI 9635 QA photomultiplier. The quartz emission was observed through a Melles-Griot blue filter (FIB002) where the wavelength (in nm) is peaked at 320-480 nm, FWHM is 80 ± 16 nm and peak transmittance (minimum) is 60%. It is also provided with a $^{90}\text{Sr}/\text{Y}$ source with a dose rate of 0.023Gy/s. All the TL measurements were performed using a linear heating rate of $5^\circ\text{C}/\text{s}$ from room temperature up to 500°C in a N_2 atmosphere (to avoid spurious TL signals). Four aliquots of 5.0 ± 0.1 mg each of this synthetic material were used for each measurement. Sample processing and measurements were made under red light to avoid the release of the trapped electrons from the semistable sites into hole centres (including luminescence centres) due to light sensitivity.

3 RESULTS AND DISCUSSION

3.1 Morphological Study

X-ray diffraction of the samples LiAlSiO_4 , $\text{LiAlSi}_5\text{O}_{12}$ and $\text{LiAlSi}_{16}\text{O}_{22}$, shows large presence of β -eucryptite with traces of β -spodumene phase. Samples poorer in aluminium and lithium elements ($\text{LiAlSi}_{16}\text{O}_{22}$) display α -quartz structure; samples with higher Li-Al content (LiAlSiO_4) show β -quartz lattices and samples with intermediate Li content produce β -spodumene that is detectable by the existence of the XRD peak at $21^\circ 2\theta$ K_αCu . The synthesised Al-Li-Si mixtures are basically Li-Al rich β -quartz, i.e., β -eucryptite. Figure 1 shows a clear evolution trend in the main XRD peak ($23^\circ 2\theta$) as it shifts to right with a decreasing amount of Li-Al in the lattice while maintaining the β -quartz structure.

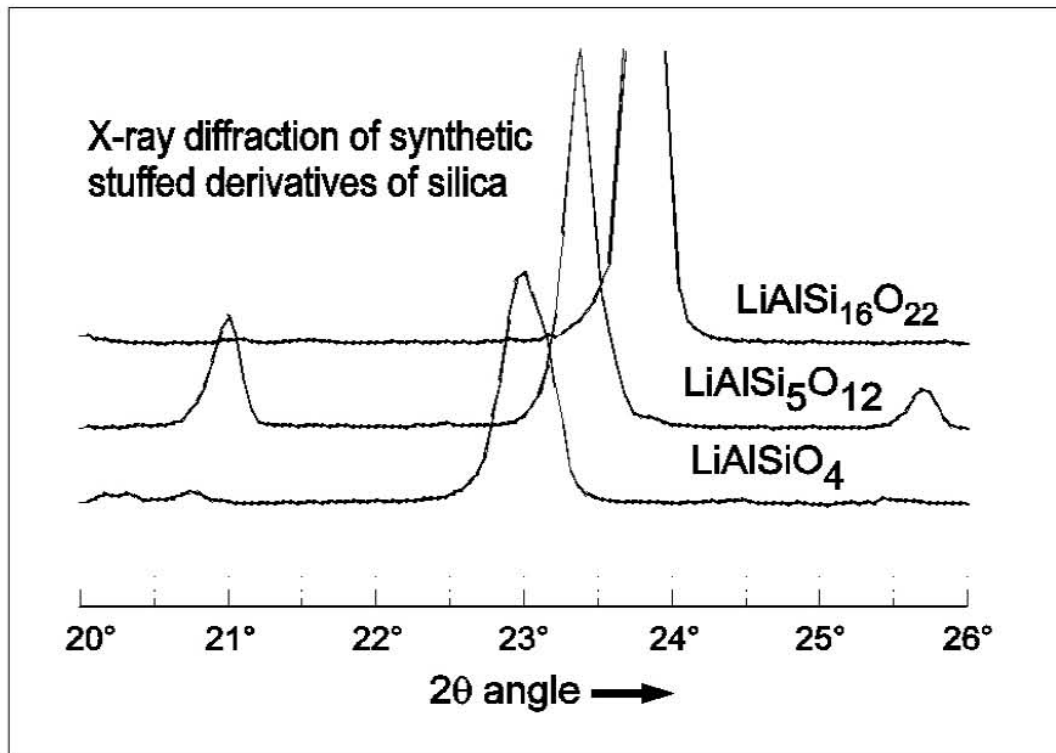


Figure 1: X-ray diffractograms of the studied materials. (Range 20-26° 2θ)

3.2 UV-blue thermoluminescence

To characterise a material as a dosimeter, its response to ionising radiation (the sensitivity to the dose) is needed. The TL glow curves of the three quartz crystals, doped progressively by Li and Al and beta irradiated with the same dose (5Gy) are displayed in figure 2.

All samples are sensitive to radiation and display an intense emission at 90°C. The group of components producing this peak is also detected in the TL glow curves obtained for different irradiated natural quartz [1] and aluminosilicates (e.g. microcline, a K-rich feldspar [7]), and are intrinsically associated with the Si-O bonds in the lattice, regardless of impurities and structural state. They do, however, show different behaviours depending on the degree of doping. The sample with the lowest Li-Al concentration clearly displays two more maxima at 130°C and 200°C besides the 90°C peak (fig 2a). At temperatures of over 300°C, no emission is appreciated. When the dopant level is increased (LiAlSi₅O₁₂), the 90°C TL emission decrease intensity (by more than 50%) and the peaks at 130°C and 200°C change shape, position and intensity. Thus, the 130°C peak is harder to detect and the 200°C peak shifts to about 240°C (fig 2b). The sample with the highest Li-Al concentration (LiAlSiO₄) has a 130°C peak that is not directly observed, and the emission is less intense than the other samples (a ratio of 7:2 respect to LiAlSi₁₆O₂₂ and 3:2 respect to LiAlSi₅O₁₂). At higher temperatures, a wide broad maximum peaking at 350°C, in a position corresponding to the 'empty' zone of the others samples, can be appreciated (fig 2c). These changes in the intensity of the TL emission lead to the conclusion that the Li-Al dopants act as powerful TL inhibitors and show the dependence of the TL signal, measured at the maximum of the main peak, on the dopant concentration.

Therefore, the material doped with the lower concentration of Li-Al is more suitable for radiation dosimetry purposes. The intensity and the shift toward high temperature in the position observed for the 200°C peak with increasing Li-Al concentration should be highlighted. This indicates high dopant levels involve a progressive generation of deeper energy traps that are emptied at higher temperatures.

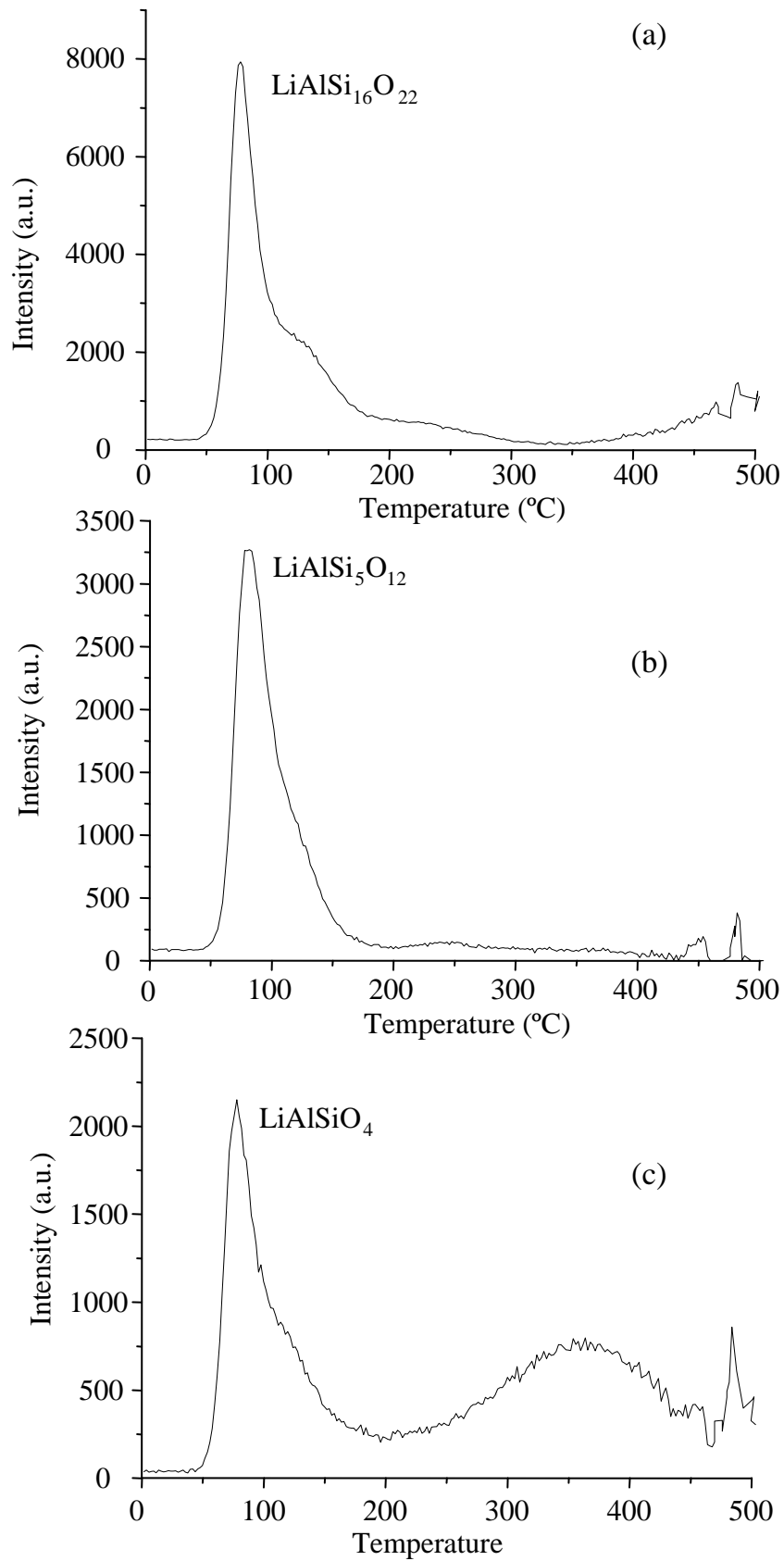


Figure 2: Thermoluminescence prompt curves of 5Gy β -irradiated synthetic quartz with different Li/Al dopant concentration. The dose rate of the $^{90}\text{Sr}/\text{Y}$ β -source was 0.023Gy/s.

Some measurements were made to determine the response of materials to the β radiation dose varying in a range of one order of magnitude (0,5 to 5Gy). The results, expressed as an integrated TL signal (area between 50-200°C) are shown in figure 3.

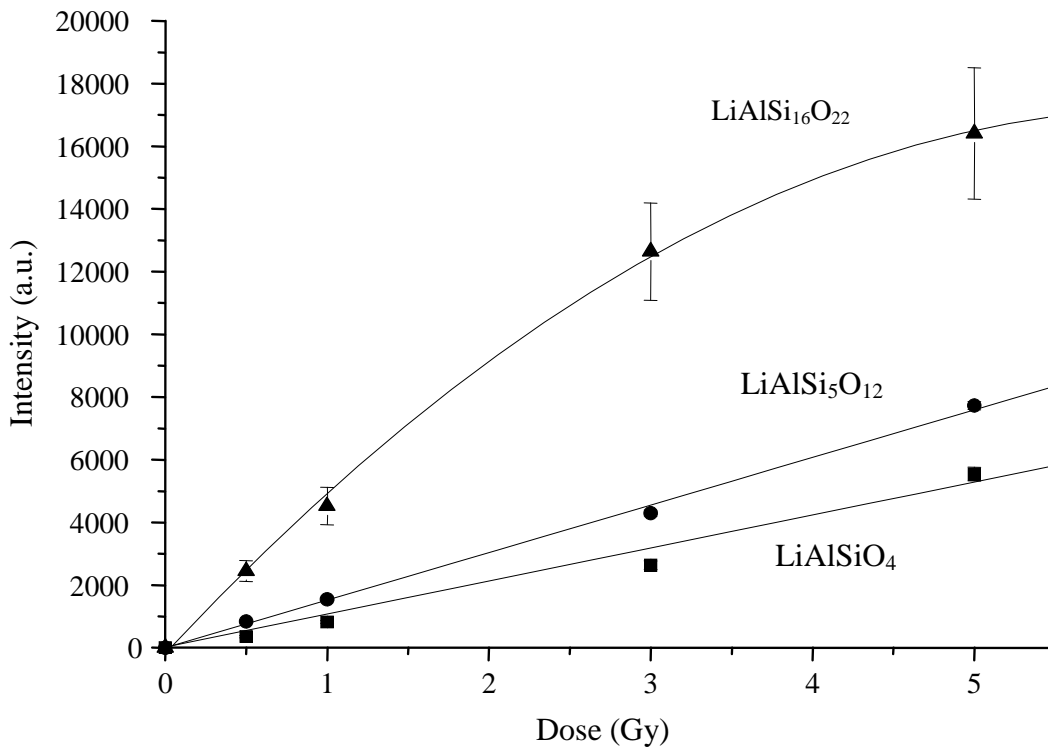


Figure 3: Dose dependence of the TL signal in the range of 0.5-5Gy for different doped synthetic quartz.

The points corresponding to the lowest dopant concentration specie (figure 3), are well fitted by a second order polynomial expression with a negative quadratic term. Thus, the dose dependence follows a saturating exponential behaviour (of which the quadratic expression is an approximation of second order) but, probably, with total saturation at doses over 5Gy (out of the range of interest for our purposes). The other two specimens not only show very good linear fitting for both, LiAlSi₅O₁₂ and LiAlSiO₄ involving the potential validity as dosimeters in the whole investigated range of doses, but also a lower dispersion in the TL signal for the samples analysed. The dispersions observed for LiAlSi₁₆O₂₂ were never lower than 12%, while values were always below 5% for other samples.

Table 1. Equation coefficients of fitting corresponding to the data of figure 3.

Sample	a	b	c
LiAlSiO ₄	-2114±2085	10954±785	---
LiAlSi ₅ O ₁₂	-44±1126	15189±424	---
LiAlSi ₁₆ O ₂₂	1891±2639	54920±3289	-4317±637

Some experiments are being carried out in our laboratory to characterise the optical and thermal fading; in the preliminary results for one week of storage, the fading behaviour is similar to that observed for other materials, i.e. a initial rapid decay and stability of the signal. Further work is still necessary to determine the evolution of the TL emission after increased periods of storage.

4 CONCLUSIONS

As in a previous work for the sample ($\text{Li}_{0.73}\text{Al}_{0.73}\text{Si}_{1.27}\text{O}_4$) [8], the three silica samples studied here ($\text{LiAlSi}_{16}\text{O}_{22}$, $\text{LiAlSi}_5\text{O}_{12}$ and LiAlSiO_4) are sensitive to radiation. Although $\text{LiAlSi}_{16}\text{O}_{22}$ dose dependence is explained by a saturating exponential equation, no saturation effect has been detected in the studied range (0.5-5Gy). All the experiments carried out confirm both samples with higher content of Li/Al could potentially be used as dosimeters in the aforementioned range as they are sensitive enough, are highly reproducible and possess good dose linearity.

In contrast, the Li-Al dopants act as powerful TL inhibitors showing the dependence of the TL signal measured at the maximum of the main peak, on the dopant concentration. Moreover, high dopant levels involve a generation of deeper energy traps emptied at higher temperatures.

5 ACKNOWLEDGEMENTS

Thanks to J.L. Robert and F. Delbove (CRSCM, CNRS, Orléans, France) for their help in mineral synthesis. We are grateful to Paul Giblin for the critical review of the manuscript and to Rafael Gonzalez for the X-ray determinations. This work has been funded by the DGICYT project PB 98-0135.

6 REFERENCES

1. V. Correcher and A. Delgado, *Radiat. Meas.* 29(3-4) (1998) 411.
2. M.J. Aitken, *Thermoluminescence Dating*, Academic Press, London (1985).
3. V. Correcher, J.L. Muñiz and J.M. Gomez-Ros, *J. Sci. Food Agric.*, 76 (1998) 149.
4. M. Martini, A. Paleari, G. Spinolo and A. Vedda, *Phys. Rev. B*, 52(1) (1995) 138.
5. D.L. Hamilton and C.M.B. Henderson, *Miner. Magaz.* 36 (1968) 832.
6. L. Bøtter-Jensen and G.A.T. Duller, *Nucl. Tracks Radiat. Meas.*, 20(4) (1992) 549.
7. V. Correcher, J. García-Guinea, A. Delgado and L. Sánchez-Muñoz L., *Radiat. Prot. Dosim.* 84(1-4) (1999), 503.
8. L. Sanchez-Muñoz, V. Correcher, J. García-Guinea and A. Delgado, *Radiat. Prot. Dosim.* 84 (1-4) (1999) 543.