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Study of luminescence, color and paramagnetic centers properties of albite

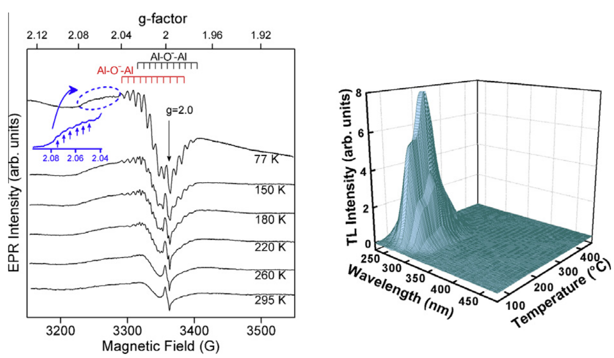
Nilo F. Cano [a,b,*], Lara H.E. dos Santos [a], Jose F.D. Chubaci [a], Shigueo Watanabe [a]

[a] *Instituto de Física, Universidade de São Paulo, Rua do Matão, Travessa R, 187, CEP 05508-090, São Paulo, SP, Brazil*
[b] *Departamento de Ciências do Mar, Universidade Federal de São Paulo, Av. Alm. Saldanha da Gama, 89, CEP 11030-400, Santos, SP, Brazil*

HIGHLIGHTS

- The TL and EPR spectra have been measured in natural albite crystal.
- Albite crystal shows TL peaks at 140, 260 and 350 °C.
- The TL emission spectrum of albite presented bands around 275, 400 and 560 nm.
- The EPR spectrum shows hyperfine lines due to Al–O$^-$–Al center superposed on Fe^{3+} signal.

GRAPHICAL ABSTRACT



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ABSTRACT

A sample of natural albite, $NaAlSi_3O_8$, from the state of Minas Gerais, Brazil, has been investigated. The mineral is a solid solution of K-feldspar (4600 ppm – K) and Ca-feldspar (1100 ppm – Ca). The TL spectra of natural and the pre-annealed at high temperature albite presented a very intense band around 275 nm and weaker bands around 400 and 560 nm. Other TL properties have been investigated through monochromatic (275 nm and 400 nm) glow curves. The EPR spectrum measured at low temperature (77 K) shows the typical 11 lines signal due to Al–O$^-$–Al center superposed on Fe^{3+} signal around $g = 2.0$. The EPR spectra above 260 K show only $g = 2.0$ signal due to Fe^{3+} ions.

Introduction

It is known that the minerals of feldspar group are the most abundant constituents of the Earth́s crust. This group is composed of alkali feldspars, plagioclase and celsian subgroup [1].

Albite or sodium feldspar of chemical formula $NaAlSi_3O_8$ belongs to alkali feldspar subgroup and is one of the end members of a series of solid solutions with $KAlSi_3O_8$ as the other end member. Solid solutions of these two feldspars are normally found in nature, but very often 5–10% mixtures of calcium feldspar are also found.

The typical structure of any feldspar mineral contains chains of SiO_4-tetrahedra in two directions perpendicular to their length, formed by the linking of horizontal rings of four tetrahedra.

As in quartz, centers related to O^-, Ti^{3+} and Fe^{3+} are found in feldspars (microclines, orthoclase, plagioclases, etc.). O^- center develops after irradiation.

* Corresponding author at: Departamento de Ciências do Mar, Universidade Federal de São Paulo, Av. Alm. Saldanha da Gama, 89, CEP 11030-400, Santos, SP, Brazil.
E-mail addresses: nilo.cano@unifesp.br, nfcano@gmail.com (N.F. Cano).

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In quartz the aluminum center results from substitution of Si^{4+} in the SiO_4 tetrahedron and after irradiation $[AlO_4/h]$ hole center is formed. This center can also be written as shown in Fig. 1(a). Oxygen belonging to two AlO_4 tetrahedron traps hole. Fig. 1(b) is the crystal structure projection in (201)-plane and only aluminum and silicon tetrahedra are shown. Symmetry centers are designated by small crosses. In Fig. 1(c) the most probable assignments of Al–O^-–Al centers are marked by heavy lines. Fig. 1(a–c) was taken from Petrov [2]. The distinct Al–O^-–Al centers are designated a_1'', C0, D0, Cm and Dm, each one depending on position of O^-. Thus a_1'', is due to O–Al, C0 to O–C0, D0 to O′–D0, Cm to O′–Cm, Dm to O′–Dm (see Fig. 1(b)).

As feldspar groups of minerals are most abundantly found in the Earth crust and as they are also used in ceramics and glass materials, they form an important class of minerals which can be used in archaeological and geological dating investigations.

In the decades of 1970 and 1980, many investigations on thermoluminescence and radiation effects related to point defects in feldspar have been carried out [3–12]. Defects have been associated with various bands in the optical spectra and the main absorption bands are in the 425–450 nm (blue) and at 700–780 nm (red) region. Telfer and Walker [13] and Marfunin [14] showed that the red band can be attributed to Fe^{3+} ions substituting Al^{3+} in a tetrahedral site. Lehman [10] and Marfunin [14] ascribed the blue band to the Al–O^-–Al center. Kirsh and Townsend [15] have proposed the following process that takes place for systems with Fe^{3+} ions under irradiation. Electrons and holes created due to irradiation are captured by Fe^{3+} and O^{2-} ions respectively. When such a mineral is heated, holes are released and recombine with Fe^{2+} ions giving rise to excited Fe^{3+} ions. On transition to the ground state, the excited Fe^{3+} ions emit red light. Furthermore, they suggest a model based on Fe ion to explain the red band (600–800 nm), whereas Speit and Lehmann [7,8] and Marfunin [14] proposed that the Al–O–Al center is responsible for the blue band (400–500 nm).

Santos and Watanabe [16] studied the effects of pre-irradiation annealing at high temperatures on optical absorption, thermoluminescence and electron paramagnetic resonance. They have observed that a pre-irradiation annealing between 800 °C/1 h and 1010 °C/1 h increases the EPR intensity of $g = 2.0$ signal with a maximum around 890 and 920 °C. Heating from 800 to 900 °C increases the magnetic dipole interaction between Fe^{3+} ions while this interaction becomes less effective for heating beyond 920 °C. Further, they have observed that a natural uncolored sample does not change color with 10 kGy irradiation. On the other hand, a 900 °C/1 h pre-heating followed by 10 kGy irradiation produces a strong absorption between 380 and 550 nm and the albite sample becomes colored with orange/red color.

Lowitzer et al. [17] carried out a combined empirical potential and density functional theory calculations of some defects in albite, such as sodium and oxygen vacancies and Schottky defects; supercell, Mott–Littleton approaches coupled to Kohn–Sham density functional method has been used.

The objective of the present work is to study the nature of the luminescence, color and paramagnetic centers in natural albite, measuring the effects of gamma irradiation and thermal treat-

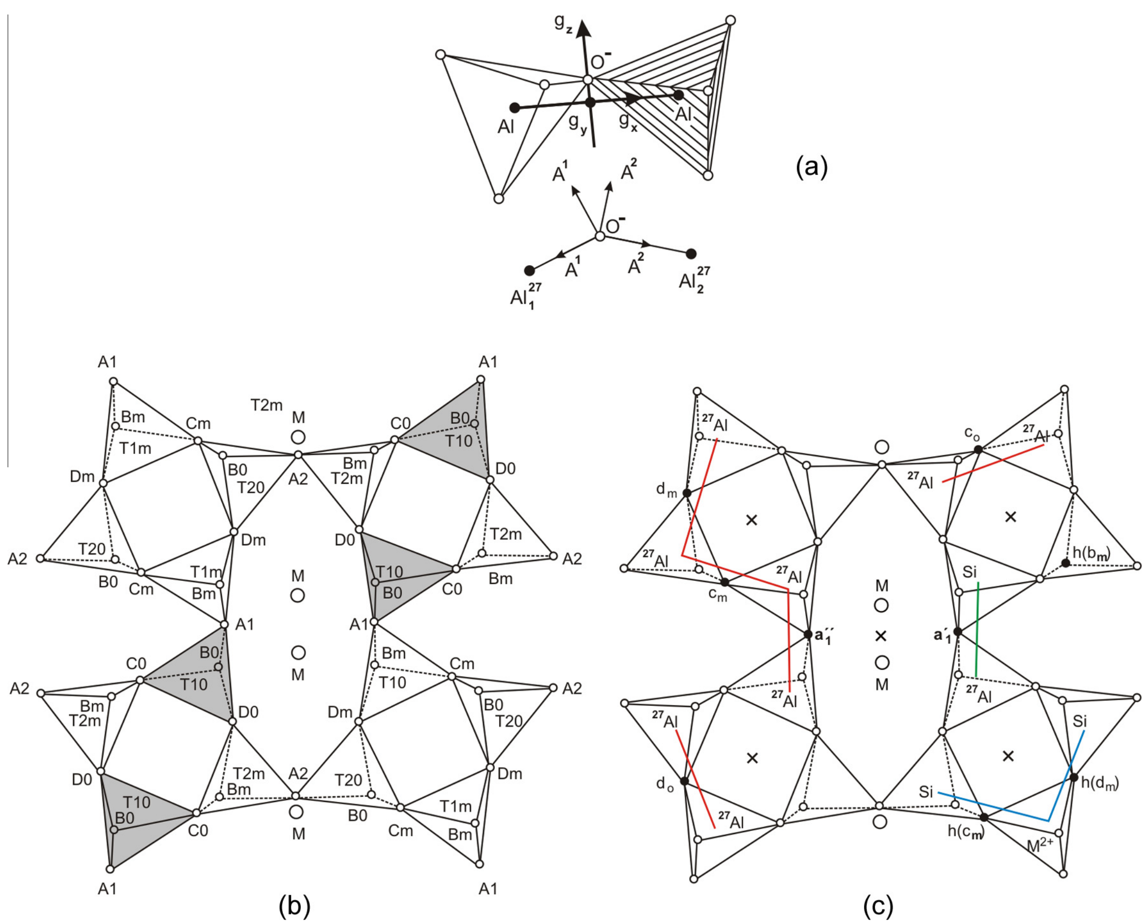

Fig. 1. Position of the Al–O^-–Al center in feldspar structure. (a) Model of the center: oxygen belonging to two AlO_4 tetrahedron traps hole with formation of O^-. (b) and (c) Projection of the crystal structure feldspar on the (201) plane. In the figure the most probable assignments of different centers Al–O^-–Al (a_1'', c_o, d_o, c_m, d_m) are marked in red. In blue are marked the most probable sites of centers SiO_4^{3-}/M^{2+}: h(b_m), (c_m) and h(d_m). In green the center Al–O^-/2Na, a_1'. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)