The Crystal Chemistry of Complex Niobium and Tantalum Oxides. IV. The Metamict State: Discussion

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Abstract

Graham and Thornber (1974b) have proposed a mechanism for metamictization in complex niobium-tantalum oxides in which complex compositions, rather than radiation damage, are the primary requirement. This note reviews the literature in support of radiation damage as a necessary condition for metamictization and suggests that the structural stability of the metamict "glass" relative to that of the crystalline pre-metamict material is an important consideration in predicting whether a substance will occur in the metamict state.

Introduction

Graham and Thornber (1974b) in an excellent study of complex niobium-tantalum oxides have proposed a new mechanism for the process of metamictization. Their model relies on the micro-exsolution of phases with similar structures in Nb-Ta oxides of complex compositions. The effect of radiation damage in the metamictization process is considered to only "accelerate the disproportionation." Although the process of metamictization is a complex one in which numerous factors must be considered, the purpose of this note is to reemphasize the importance of radiation damage in the metamictization process, particularly for the complex, orthorhombic, $AB_2O_x$-type Nb-Ta-Ti oxides, as well as to suggest that the structure of the metamict glass relative to that of the premetamict crystalline material is an important consideration in evaluating whether a substance may occur in the metamict state.

Metamictization in Complex, Orthorhombic $AB_2O_x$-type Nb-Ta-Ti Oxides

In Table 1, compositional data demonstrate the importance of uranium and thorium in the process of metamictization of complex $AB_2O_x$-type Nb-Ta-Ti oxides. Although the data in the literature are limited, in general those specimens of euxenite, fersmite, aechynite, and lyndochite which are found in the crystalline state have distinctly lower uranium and thorium contents than their metamict eucxenite and aechynite counterparts. A similar relation has been demonstrated for zircons by Holland and Gottfried (1955). Graham and Thornber (1974b) have rightly pointed to structural and compositional mechanisms for metamictization in complex Nb-Ta oxides; but these models cannot be separated from the necessary catalytic effect of radiation damage. The heart of the difficulty in understanding the process of metamictization lies in evaluating the interaction of alpha particles with different structures and compositions.

Hamberg (1914) was the first to suggest that metamictization is caused by irradiation of substances by particles which originate in the decay of radioactive isotopes of the uranium and thorium series within a crystal structure. Later work by Mügge (1922), Von Stackelberg and Rottenback (1940), Morgan and Auer (1941), Kostyleva (1954), and Holland and Gottfried (1955) supports this theory, but the mechanism of the interaction of alpha particles with the target material may vary.

Three effects are responsible for radiation damage: (1) a high velocity alpha particle may dissipate energy by excitation of electrons and ionization of atoms along its path, (2) a low velocity alpha particle may lose energy by collision, and (3) the energy of the alpha particle may be dissipated in the form of heat, resulting in a thermal spike which can reach temperatures of $10^4$K for periods of $10^{-11}$ seconds along the path of the alpha particle. The last two effects are considered important in causing radiation damage (Chadderton, 1965). The collisions cause dislocations and Frenkel defects. Solidification of the material in the thermal spike area may result in: (1) a glass (Ueda, 1957); (2) finely crystalline component oxides (Ueda, 1957; Lipova, Kuznetsova, and Makarov, 1965; Makarov, 1970); (3) the original