EGU General Assembly 2020

中国科学院地质与地球物理研究所
Institute of Geology and Geophysics, Chinese Academy of Sciences
中国科学院地球科学研究院
Innovation Academy for Earth Science, CAS

The chemical state and occupancy of radiogenic Pb, and crystallinity of RW-1 monazite revealed by XPS and TEM

Xu Tang, Qiu-Li Li, Bin Zhang, Peng Wang, Li-Xin Gu, Xiao-Xiao Ling, Chen-Hui Fei, Jin-Hua Li

Electron Microscope Laboratory,

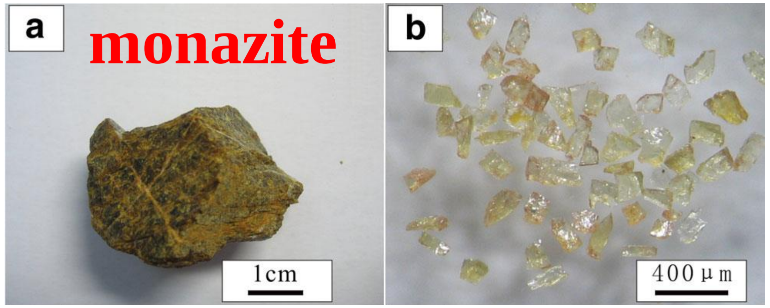
Institute of Geology and Geophysics, Chinese Academy of Sciences, China

May 6th, 2020

Outline

1. Background
2. The chemical state of radiogenic Pb
3. The Chemical, mineralogical features and structure of RW-1 monazite
4. The occupancy and distribution of Pb and Th
5. Conclusions

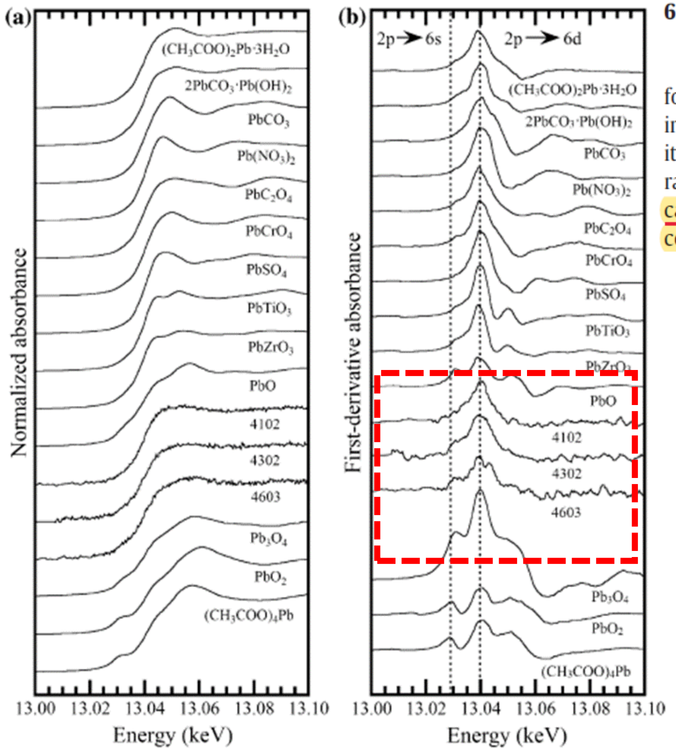
1. Background



***in-situ* dating for monazite**

The mobilization and distribution of radiogenic Pb + **The crystallinity of monazite**

The chemical state and occupancy of radiogenic Pb



Tanaka K. et al. Phys Chem Minerals (2010)

6. Consequences

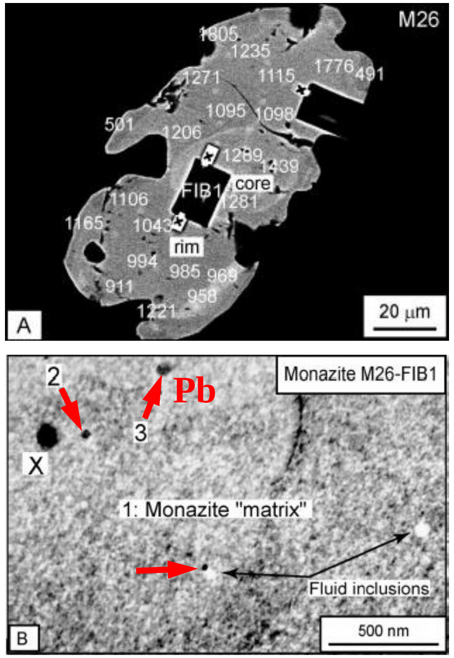
A tetravalent state of radiogenic Pb has important consequences for its compatibility in the zircon lattice. Common Pb is notoriously incompatible in zircon (see Watson et al., 1997), the main reason for its datability by the U–Pb method. That is understandable from the ion radii shown in Table 1. It is also clear from this table that tetravalent Pb can substitute even better for Zr than U or Th, and should be highly compatible in zircon.

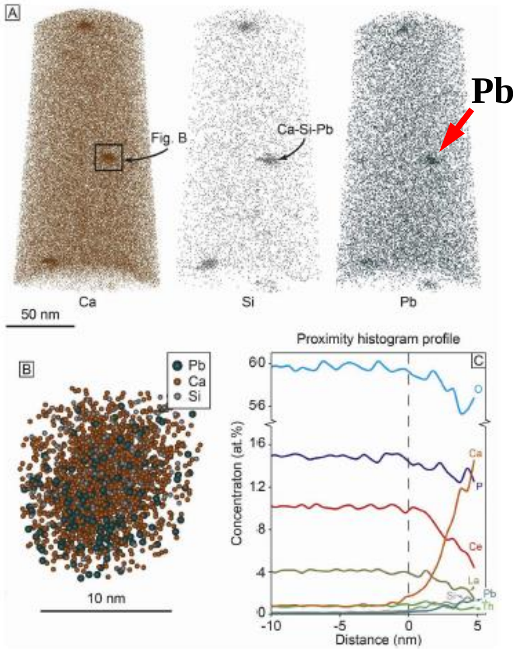
J. Kramers et al. Chemical Geology. (2009)

(1) Pb^{4+} or Pb^{2+} ?

(2) Inconsistent ages.

Why?





Seydoux-Guillaume A.M., et al. Geology (2003); Fougerousea D. et al. Chem. Geol. (2018)

- **The chemical environment (valence and occupancy) of radiogenic Pb in monazite down to nanometer and atomic scale need further investigation.**

2. The chemical state of radiogenic Pb

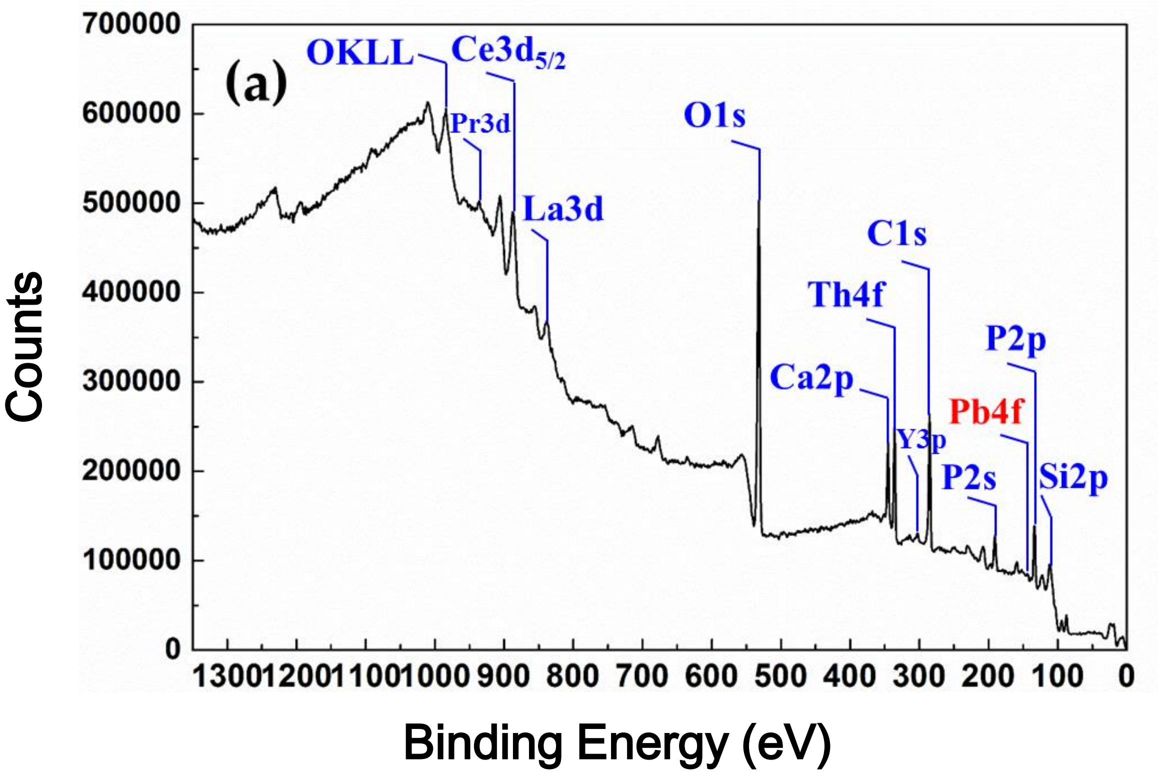


Table 1 Binding energies (eV) of Pb 4f for RW-1 monazite, PbO, Pb_3O_4 and PbO_2.

B.E. (eV)	Chip1	Chip2	PbO	Pb_3O_4	PbO_2
Pb $4f_{7/2}$	138.16	138.04	138.0	137.4	137.3
Pb $4f_{5/2}$	143.02	142.9	142.9	142.2	142.1

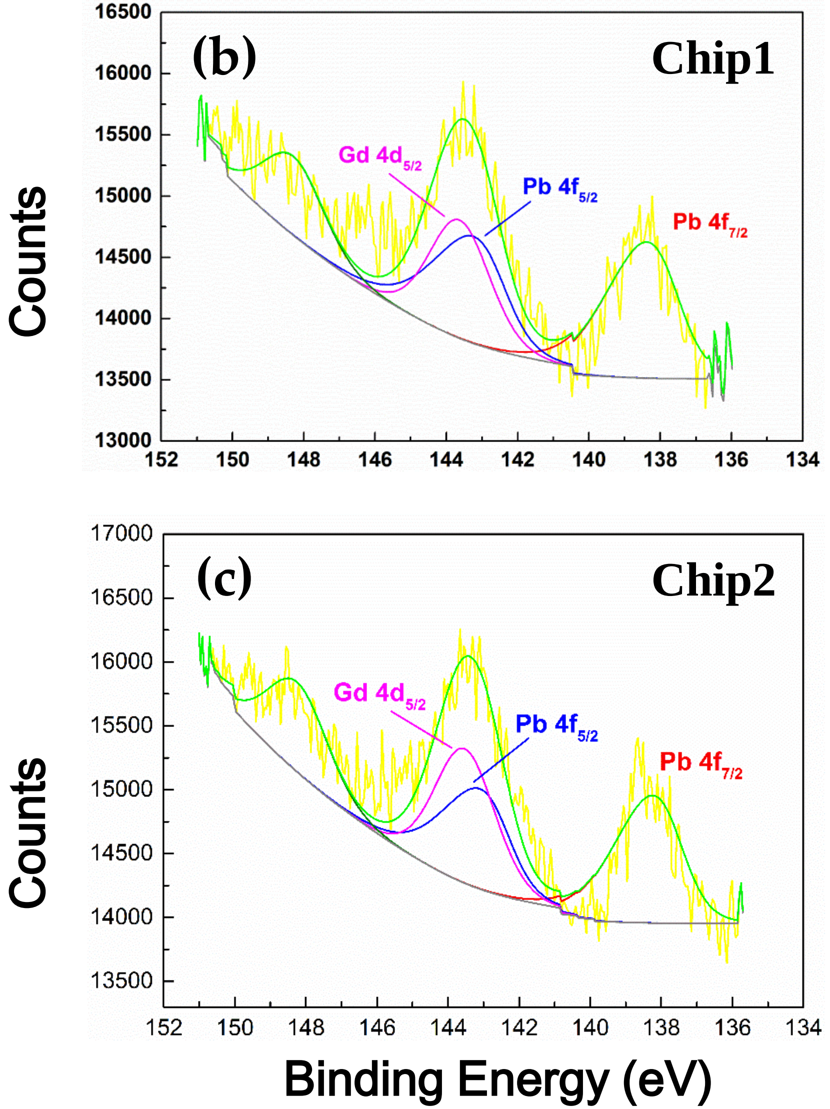
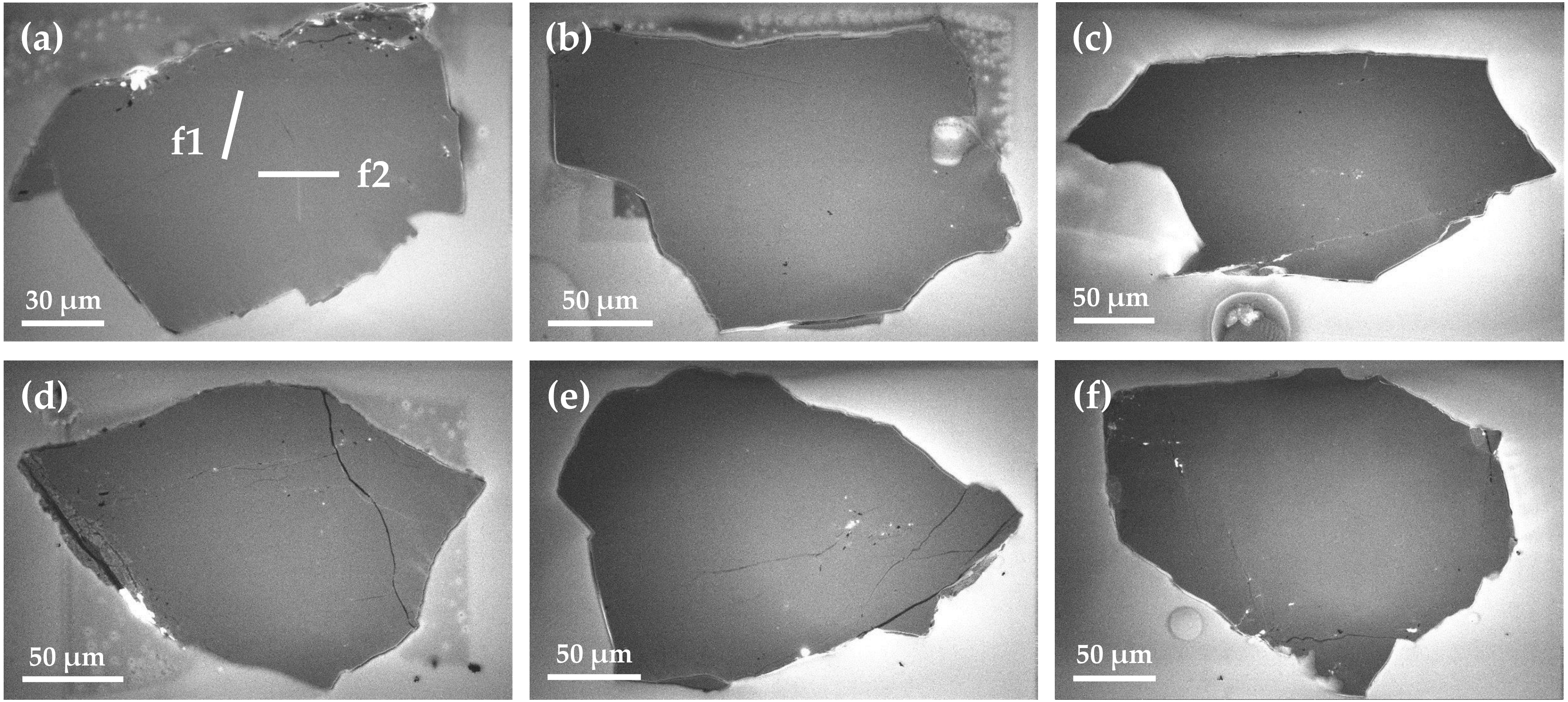
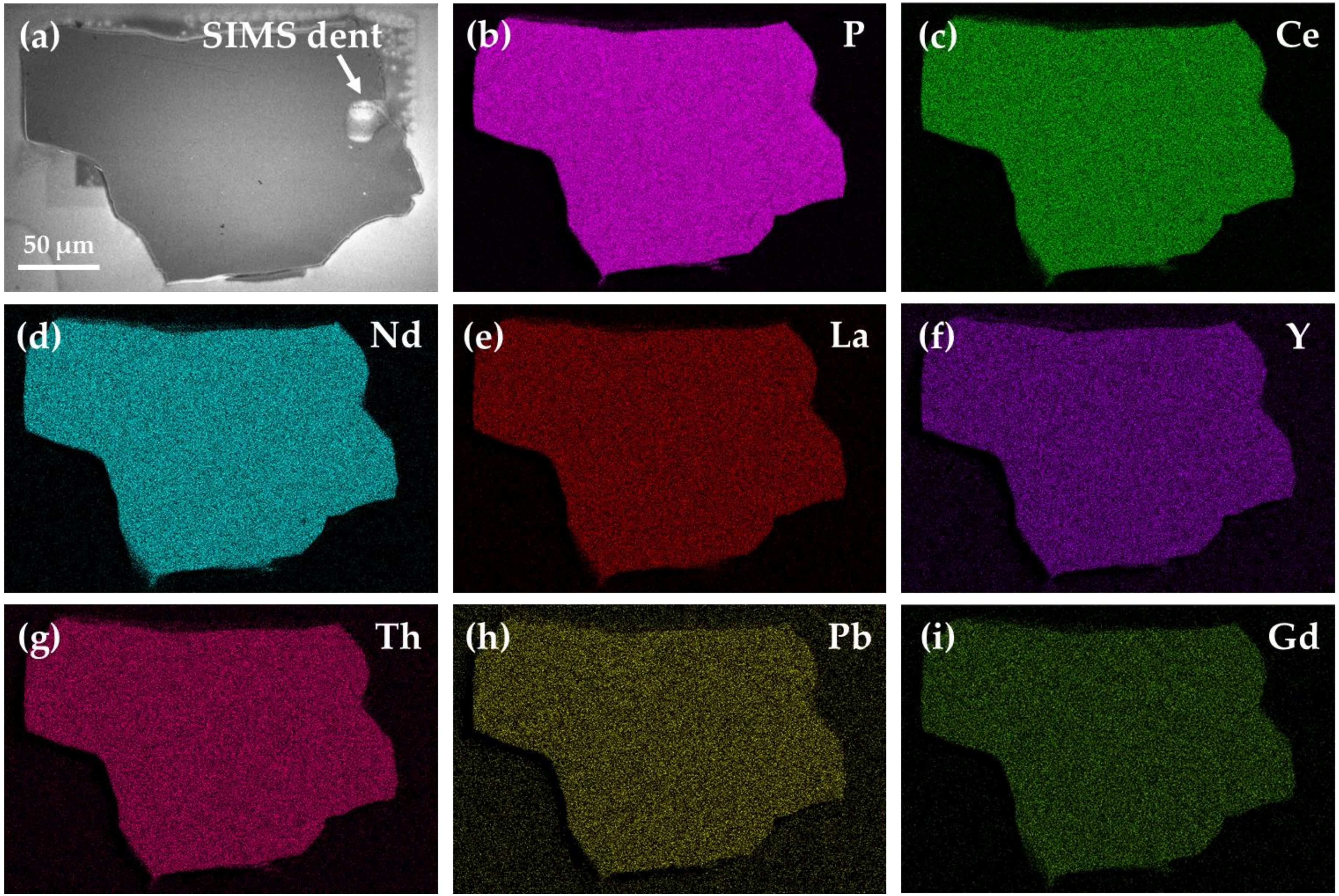


Fig. 1 (a) The full XPS spectra (survey). (b-c) The Pb 4f XPS spectra and fitted peak for the natural monazite.

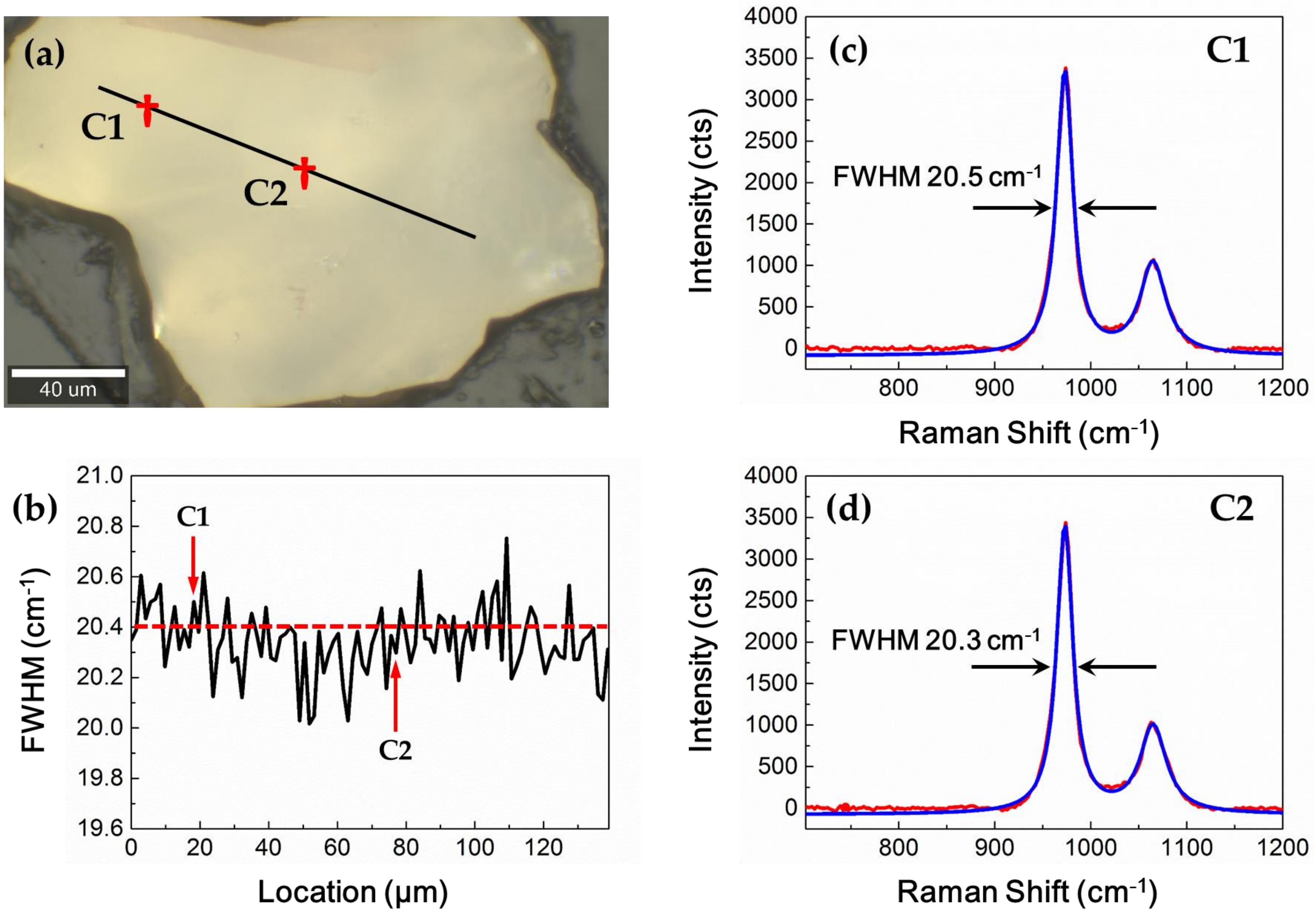
3. The Chemical, mineralogical features and structure of monazite



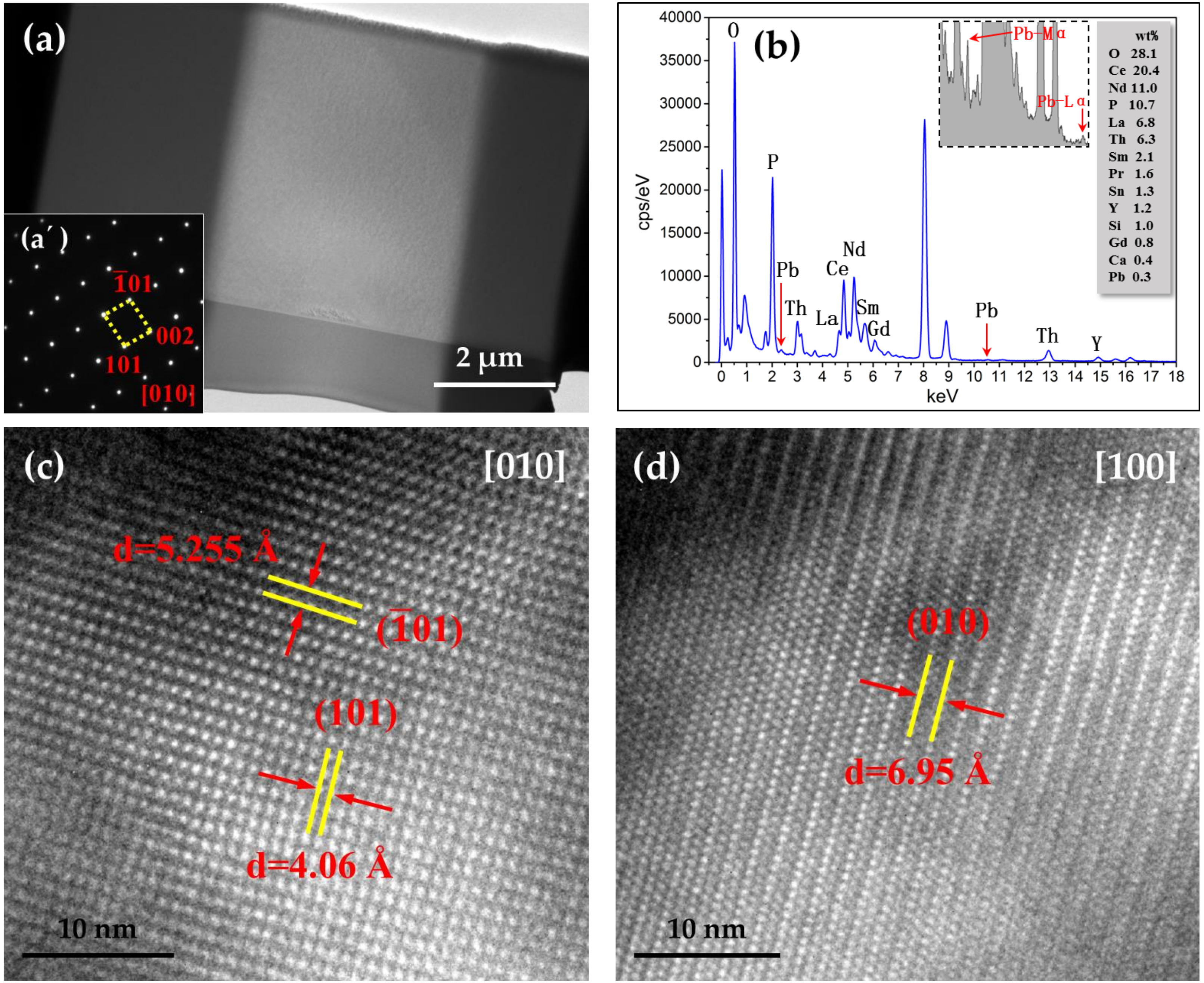
The CL images show that dark–bright contrast is uniform and there is no oscillatory zoning, suggesting that the elements in the monazite are homogeneous distribution at the micrometer scale.



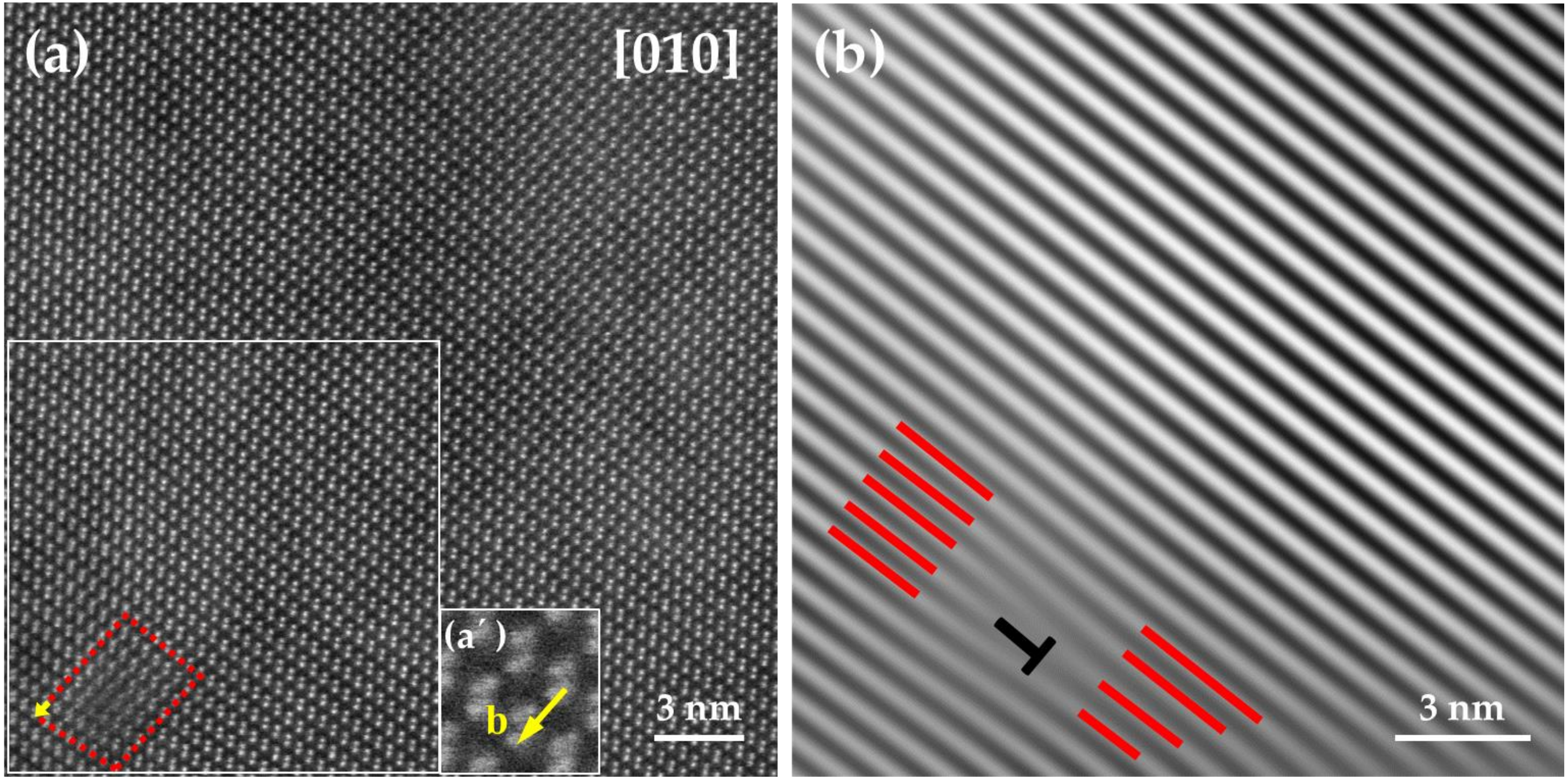
The EDS maps show a homogeneous distribution of elements in this monazite as well.



The Raman spectra shows a broadened Raman band with FWHM around 20.4 cm^{-1}, which is much wider than those (7.2 cm−1) of annealed monazite and implicating that the sample experienced with radiation damage.

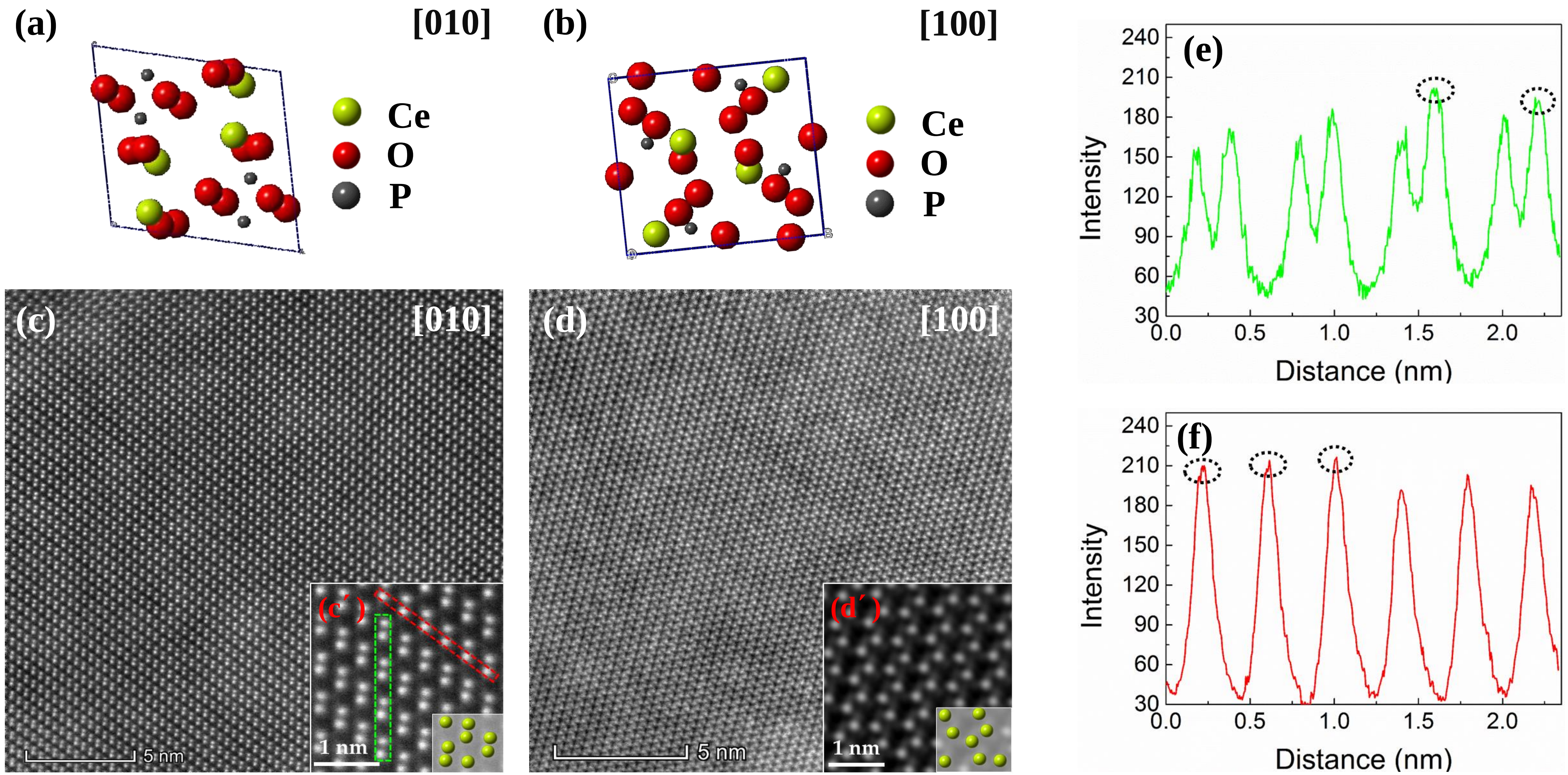


Selected area electron diffraction (SAED) image and HRTEM images demonstrated that the monazite we studied is well crystalline.



Some distrored lattices was also observed, such as edge dislocations. The edge dislocations marked with black ⊥ sign were seen clearly, gliding on (111) planes and Burgers vectors b=[10-1]. The edge dislocation is probably related to the radiation damage induced by alpha decay and resulted in the broadening Roman band.

4. The occupancy and distribution of Pb and Th



By comparing the arrangement of bright atomic columns in HAADF images with the atomic arrangements of $CePO_4$, there is a one-to-one correspondence was found between bright atomic column and Ce site, suggesting the heavier species substitute the Ce site in the monazite structure.

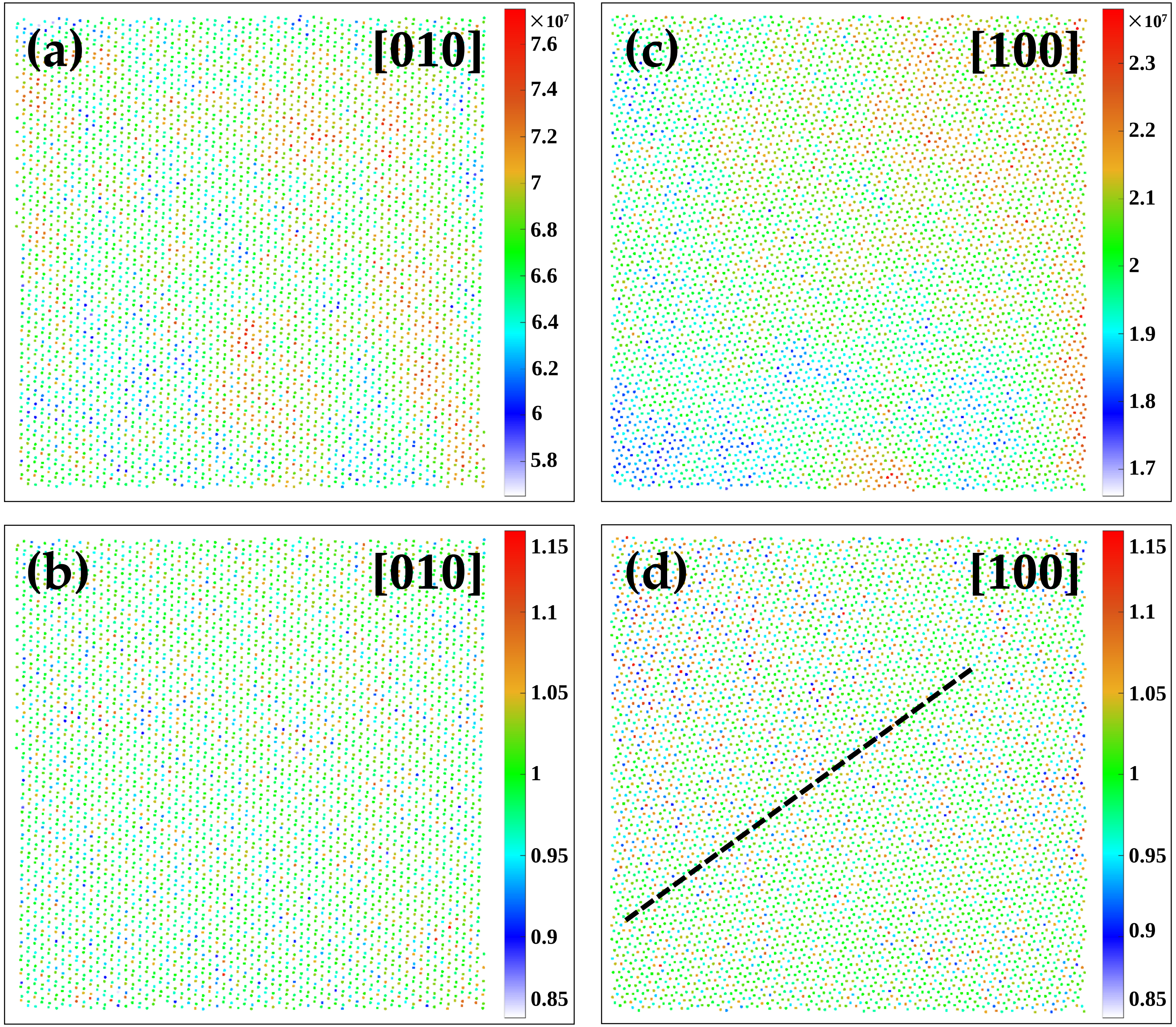


Fig. 8 The integral intensity mapping and normalized intensity mapping of STEM-HAADF image (as shown in Fig. 7c and 7d) along [010] and [100] direction, respectively.
(a, c) The integral intensity mapping with color bar from blue to red and up to yellow roughly reflect the additive intensity of heavier elements at Ce site or atomic column.
(b,d) The normalized intensity mapping with different colors reflects the relative concentration of radiogenic Pb and Th in each columns. The average value is set to be 1.0 (green), Blue-to-white (value is 0.85) represents the distribution of REEs where Pb and Th is poor, and red-yellow (1.15) represents the distribution of Pb-rich and Th-rich in the column.

5. Conclusions

(1) The TEM and STEM-HAADF data demonstrated the studied natural monazite is well crystalline in most area. Meanwhile some distorted lattices induced from self-radiation was also observed, which resulted in broadening band of RM analysis.

(2) The radiogenic Pb exists as Pb2+ in current state.

(3) The STEM-HAADF data revealed that Pb atom substitute for the Ce atoms within the monazite crystal lattice. A normalized intensity mapping was developed for the STEM-HAADF images to better visualize the distribution of Pb and Th.

Email: tangxv@mail.iggcas.ac.cn

Thank you for your attention!